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DEVELOPMENT OF HIGH TEMPERATURE SUPERCONDUCTOR/METALLIC CONDUCTOR CONTACTS FOR HIGH CURRENT APPLICATIONS IN THE POWER SYSTEM (PART I)

METALLIZING TECHNIQUE

Report No. 91-52-K

A.V. Manolescu, P. Mayer, S. Krishnasamy,
E. Di Blasio and M. Eygenraam

ABSTRACT

High temperature superconducting (HTSC) devices for high current applications have to interface with the conventional, non-superconductor (metallic conductor) part of the power system. Since the interface between the ceramic superconductor and metallic conductor is a topic that received very little attention until recently, a program with the objective to develop high performance HTSC/metal contacts was selected for 1989 Director's Funding. As part of this program, a method to fabricate the ceramic superconductor, $YBa_2Cu_3O_{7-x}$, was developed. An "in-house" metallizing technique to join the ceramic and metallic materials was formulated and the performance of the contacts engineered at OHRD's laboratory and by commercial suppliers was tested. The results to date indicate that the superconductor samples metallized at OHRD's laboratory exhibited superior metallurgical, electrical and mechanical performance.

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EXECUTIVE SUMMARY

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METALLIZING TECHNIQUE

A.V. Manolescu, P. Mayer, S. Krishnasamy,
E. Di Blasio and M. Eygenraam

Successful application of High Temperature Superconductor (HTSC) materials in power systems depends on the progress in the development of suitable conductors with adequate strength to withstand operating stresses, to resist environmental attack, and to be compatible with metallic conductors.

As part of the Research Division's contribution to assess the potential applications of HTSC in Ontario Hydro's power system, a program with the objective to develop high performance contacts between ceramic HTSC and metallic conductors was selected for the 1989 Director's Funding.

To achieve this objective, an affordable and simple procedure to fabricate dense ceramic superconductor, ($YBa_2Cu_3O_{7-x}$ (1-2-3) compound) was developed. Samples needed for this investigation were fabricated using the developed method based on the solid state reaction between component oxides at elevated temperature.

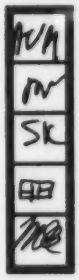
Based on literature review and the project team's expertise, the contact material and the technique to connect the ceramic 1-2-3 samples and the conventional metallic conductor were selected. Silver was the selected contact material, because of its low oxygen affinity, good electrical conductivity, superior mechanical properties and lack of interaction with the ceramic superconductor. The new technique to join the HTSC and the metallic conductor was a two stage process. In the first stage, a thin layer of silver that has compatible properties with the ceramic superconductor was deposited by metallization, on the 1-2-3 sample. The second stage consisted of joining the metallized sample with the metallic conductor (lead-wire) by soldering. Metallizing procedure was used to deposit the silver layer, because this technique is suitable for joining materials with different thermal expansion characteristics. From a large number of available techniques to metallize the ceramic substrate, five methods were tested. These techniques were: Ag-epoxy painting, thermal deposition, sputtering, thermal spraying (flame spray and plasma arc spray), and pressing/sintering.

The HTSC/silver contacts deposited in OHRD's laboratory using the selected techniques, as well as those fabricated by METCO Canada, CPS Superconductor Corporation and Perkin Elmer in the USA were evaluated by laboratory testing. Because most of the silver contacts exhibited very poor mechanical properties and their application procedures required expensive instrumentation, extensive work has been

carried out in our laboratory to develop inexpensive and reliable contacts. As a result, a new metallizing technique was developed to deposit silver contacts on 1-2-3 samples. This technique consisted of pushing a Ag-epoxy slurry through a silk-screen or stencil-type mask depending on the required thickness of the contact layer. After deposition, the samples were cured, sintered at 900 C and annealed in flowing oxygen for 18 hours at 560 C. The metallic conductors, the lead-wires, were then joined with the metallized superconductor by soldering. Since the preliminary testing showed that these contacts exhibited good mechanical properties we used only the "in-house " technique to prepare samples for further assessments.

Metallographic, electrical and mechanical tests were carried out to assess the performance of the contacts deposited by the "in-house" metallizing technique. The results of these tests demonstrated conclusively that this technique produced reproducible and very reliable contacts. The 1-2-3 samples exhibited a very sharp transition temperature at 90 K. The electrical resistivity of Ag/HTSC contact was exceptionally low, ranging from 10^{-8} to $10^{-9}\Omega.cm^2$ and easily reproducible. Metallographic examination showed that the silver contact has excellent adherence to the ceramic substrate under normal environmental and thermal cycling conditions. The silver contact was chemically inert since it didn't interact with the superconductor material. However, experiments carried out under controlled environment containing $^{13}CO_2$ showed that the ceramic superconductor samples were susceptible to the attack by condensing moisture and carbon dioxide. Therefore, procedures to protect the surface of the superconductor samples must be developed before any electrical device or component based on HTSC materials is built in the future.

The results presented in this report demonstrate conclusively that the new metallizing technique produces the reproducible and high quality contacts/joints required for practical applications of HTSC in the power systems. The laboratory testing carried out to establish the current carrying capacity of the developed contacts and the work to demonstrate the fault current limiting ability of the metallized samples are now completed and will be reported separately.



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To Dr. D. Mills
Director of Research

DEVELOPMENT OF HIGH TEMPERATURE SUPERCONDUCTOR/METALLIC CONDUCTOR CONTACTS FOR HIGH CURRENT APPLICATIONS IN THE POWER SYSTEM (PART I)

METALLIZING TECHNIQUE

1.0 INTRODUCTION

Dreams and hopes of finding superconductors with high critical transition temperature were renewed in 1986 when K.A. Mueller and J.G. Bednorz of IBM's Zurich research laboratories discovered that a ceramic material consisting of oxides of lanthanum, barium and copper becomes superconductor at 30 K. By February 1987, P. Chu and M.K. Wu's discovery of yttrium barium copper oxide compound superconducting at 95 K brought the transition temperature into the range suitable for liquid nitrogen cooling. This unexpected breakthrough initiated a new era in the development high temperature superconductors. To date, the HTSC materials are defined as complex ceramic oxides that become superconductors above 25 K. The general aspects of superconductivity, the history of discovery of superconductive compounds and their basic properties (Figures A1 to A4), the most common classification of HTSC materials and some background information on the $YBa_2Cu_3O_{7-x}$ compound (Figures A5 and A6) are briefly reviewed in Appendix A. More detailed information on superconductivity,in general, and HTSC materials in particular, is provided in references/1-9/.

As part of the Research Division's effort to assess the potential applications of superconductive materials in Ontario Hydro's power system, a program with the objective to develop high performance HTSC/metal contacts was selected for 1989 Director's Funding/1/. It was anticipated that at the completing time of the program a fully characterized and tested prototype contact would be delivered. The immediate identifiable benefits of the program included: contribution to the development of a laboratory prototype contact, development of expertise in the area of metallizing ceramic materials and understanding of environmental behaviour of HTSC and electrical contacts in general. The program was initiated in January 1989 and completed in two years, (i.e. end of 1990).

This report describes the developed metallizing technique and the laboratory tests devised to assess the contact performance. The results of these tests are also summarized. However, the experimental work that was carried out to establish the current carrying capacity of these contacts and to assess the fault current limiting function of metallized 1-2-3 samples are being reported separately.

2.0 EXPERIMENTAL

2.1 Objective and Method of Approach

The objective of the overall program was to deliver a characterized and tested prototype contact between HTSC material and metallic conductor for power system applications. The objective of this part of the program was to develop the joining technique for HTSC and metallic materials.To achieve this objective, the following method of approach was chosen:

- Review the literature and identify the potential materials and techniques to join ceramic superconductors and metallic conductors.
- Fabricate the ceramic superconductor material and samples.
- Select the best candidate materials and techniques to engineer the contacts.
- Develop the testing procedures.
- Test the performance of the contacts.

2.2 Materials and Techniques

2.2.1 Preparation of Ceramic Superconductor Samples.

Because $YBa_2Cu_3O_{7-x}$ has a relatively high transition temperature (90 K), it was chosen as the base superconductor material for this investigation. Based on the analysis of quoted costs of commercially available HTSC samples across North America and our costs, it was established that it was cost effective to fabricate the superconductor material in our laboratory.

The $YBa_2Cu_3O_{7-x}$ (1-2-3) compound, was prepared by solid state reaction between Y_2O_3, $BaCO_3$, and CuO powders as described in a previous report/8/. This process consists of milling together the powdered reactants, followed by calcining the resulting mixture at 915 C for 18 hours and annealing for 6 hours at 545 C in oxygen. These operations were repeated three times to insure the homogeneity of the product. The resulting compound was pulverized and sieved to the desired particle size. This powder was then pressed into rectangular bar-shaped samples at a pressure of 20,000 psi. The samples were then sintered for 18 hours at 945 C and annealed in flowing oxygen for 18 hours at 540 C.

2.2.2 Sample Configuration

The ceramic samples used for metallizing and testing are illustrated schematically Figure 1

2.2.3 Joining Technique

Based on extensive literature review and the project team's expertise, a two-stage joining method was formulated. Figure 2 illustrates the concept of the proposed method.

In the first stage a thin layer of a metal, that has engineering properties compatible with the

ceramic superconductor, was deposited on the 1-2-3 sample by metallization. Since the metal deposited on the ceramic sample is thin and ductile enough to deform plastically with dimensional changes of the substrate, the metallizing technique is well suited for engineering interfaces between materials with different thermal expansion characteristics.

Silver was selected as the metallizing component for the 1-2-3 ceramic sample, because of its unique material properties. Simple thermodynamic analysis based on the diagram of free energy of oxide formation (Figure 3) indicates that copper and the metals lying below it on this diagram have a relatively low energy of oxide formation and therefore a high affinity for oxygen and most probably will interact with the ceramic superconductor/4/. This interaction would result in oxygen depletion of the ceramic superconductor leading to loss of its superconductivity. Silver is the only practical choice of a metal that lies above copper on this diagram; gold and platinum can not be considered because of economical reasons and palladium because of its known interaction with the 1-2-3 compound. This diagram also indicates that silver/silver oxide system may act as a buffer system since the silver oxide can easily dissociate to provide the oxygen required to maintain the stoichiometry of the 1-2-3 ceramic. Silver has good mechanical and electrical properties suitable for practical power system applications.

The second stage of the proposed method consisted of connecting the metallized ceramic superconductor with the metallic conductor by suitable means.

Metallization Procedure

The metallization procedure consisted of cleaning the ceramic samples, masking their surface to achieve the required configuration of the contacts and silver deposition. After fabrication, the surface of the 1-2-3 samples was abraded with a 240 grit silicon carbide paper to remove the degraded superconductor layer that forms due to its interaction with atmospheric moisture and to increase the surface area of the ceramic substrate. Since a four-point method is used to evaluate the electrical properties of the metallized samples, four contacts were deposited on each sample through a suitable mask. Figure 4 shows the configuration of the contacts that were used for this investigation.

From a large number of commercially available methods to metallize ceramic materials, five techniques- Ag-Epoxy deposition, thermal deposition, sputtering, thermal spraying (flame spray and plasma arc spray) and pressing/sintering -reported in the literature to provide good electrical contacts were selected for trial/9-15/. These techniques are listed in Table 1. After metallization procedure was completed, the silver lead-wires (metallic conductor) were attached to the metallized areas of the ceramic. Since most of the silver contacts deposited by these techniques separated easily from the ceramic substrate during the lead-wire soldering procedure, and the deposition procedures required expensive instrumentation not available at the time we performed this investigation, extensive work was carried out in our laboratory to develop a reliable metallizing technique. As a result, a new metallizing technique was formulated and developed for depositing silver contacts on 1-2-3 samples. This technique is described in the next section.

Description of the "In-House" Developed Metallizing Technique

The technique developed in OHRD's laboratory consists of forcing a Ag-epoxy slurry, commercially available as Epo-Tek H20S, through a suitable mask wrapped around the 1-2-3

sample to achieve the required configuration of the electrical contacts. Depending on the slurry fluidity, silk screen or stencil-type masks have been used in these experiments. Through trials, it was established that the initial thickness of the Ag-epoxy slurry that was pushed through the mask on the surface of 1-2-3 sample, was the determining factor of reliability of the deposited contacts. After the slurry was deposited, the samples were cured at 172 C for two minutes and sintered at 900 C for six hours. The samples were then cooled down to 560 C and annealed at the same temperature for 24 hours in flowing oxygen. The annealed samples were then cooled to the room temperature and stored in a desiccator to prevent the environmental attack.

Attachment of Metallic Conductor to the Metallized Ceramic

Following the metallization procedure, silver lead-wires were attached to the metallized superconductor. Two methods have been experimented with wire attachment:

- soldering technique using different solder alloys, and

- pasting with Ag-epoxy followed by annealing of HTSC/Ag-contact/solder alloy/lead-wire sample

It was established that the soldering procedure was the better method of attaching the lead-wires and therefore, this technique was used to prepare the samples for the laboratory testing of contact performance.

2.3 Contact Testing Procedures

2.3.1 Testing Approach

The following criteria were used to assess the contact reliability:

- Electrical Performance The contact must tolerate the current flow between two materials with different carrying capacities. The contact resistance, must be three or four orders of magnitude below that obtained with currently available contacts, to prevent sample deterioration due to localized heating from the higher current density.

- Metallurgical Performance The contact metals should minimize the stresses from differential thermal expansion of the two components, provide epitaxial bonds without introducing surface defects and ensure the physico-chemical stability (stoichiometry of ceramic 1-2-3 superconductor and resistance to environmental attack) of the contact.

- Mechanical Performance The contact should provide a good adherence between the two components under thermal cycling from room temperature to liquid nitrogen temperature and resist operating stresses.

2.3.2 Test Description

Based on these criteria, standard and newly developed laboratory tests were carried out to characterise the performance of the samples that were metallized in our laboratory. In parallel, samples fabricated and metallized by commercial suppliers were also tested for comparison with

the "in-house" fabricated and metallized samples.

Metallographic Analysis

Optical and Scanning Electron Microscopy (SEM) were used to characterize the microstructure of 1-2-3 compound and the adherence between Ag-contact and the ceramic sample and between solder alloy and silver contact. The information obtained from the metallographic analysis of investigated samples is summarized in Table 2. Standard metallographic techniques consisting of sectioning the samples, cold mounting, grinding and polishing, were used to prepare the samples for examination under the optical microscope. Both, the metallographically prepared and fractured by bending samples, were used for examination under the SEM. The elemental composition of these samples was analyzed with an Energy Dispersive X-Ray Analyzer (EDX) system attached to the SEM.

Surface Analysis

Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS) and Electron Spectroscopy for Chemical Analysis (ESCA) techniques were used to analyze the chemical stability of the system components at both, Ag-contact/1-2-3 sample and solder alloy/Ag-contact interfaces and the effect of atmospheric and cryogenic conditions on metallized sample integrity (Table 2). These analyses were performed on the following type of surfaces: those of cross sectioned and metallographically prepared samples, of metallized samples, and on that of the superconductor that was fractured when the lead-wires and the contact layer were pulled away. These analyses were performed at Surface Science Centre, University of Western Ontario.

Electrical Measurements

To characterise the electrical performance of the investigated samples, the electrical resistivity of the 1-2-3/Ag contacts deposited by different techniques, (Rc), the critical transition temperature (T_c) and critical current density (J_c) of the 1-2-3 superconductor were measured on the freshly metallized samples. To prevent the possible degradation of the superconductor material due to interaction with atmospheric humidity, before and after each measurement, the metallized samples were stored in a desiccator.

The sample configurations that were used to measure the electrical properties of metallized 1-2-3 samples are shown in Figure 5. A power supply, Kepco OPS 150 V 1.5 A for low current, or 1210-s Lambda LLS 9008 designed for up to 100 A, and a Hellwett Packard 3457 Digital Multimeter were used for electrical measurements (Figure 6). During the testing procedure the metallized sample was mounted in a copper holder designed such that the sample could be subjected to both, laboratory environment and liquid nitrogen without the need for remounting. A type T thermocouple was used to measure the temperature of the sample. The test procedure was automated using an IEEE-488 interface bus with an IBM-AT computer.

For clarity, the graphical methods used for electrical measurements are briefly described in Appendix B and illustrated in Figures B1 and B2. The contact resistivity was determined by using the three-point method (Figure 5B) and comparing the voltage drop with and without current to eliminate any offset voltages in the multimeter. The critical temperature of the 1-2-3 superconductor was established from the changes in the sample resistivity by varying the test

temperature from room temperature to 77 K temperature (Figure 5A). The method used to measure the critical current density consisted of establishing the I-V characteristic in the standard 4-point configuration with the sample immersed in the boiling liquid nitrogen to eliminate the effect of Joule heating of the contacts on the experimental results. The test consisted of increasing the test current applied to the sample and determining the current intensity required to generate a voltage of 1μV per 1 cm of sample/16/. This is the criterion used to establish the transition from the superconducting to normal state. The value of this current, the critical current, divided by the cross sectional area of the sample gives the critical current density of the superconductor sample.

Mechanical Integrity - Contact Adherence

Optical Microscopy, SEM, and surfaces analysis techniques were used to asses the structural integrity of the samples and the adherence of the contacts to the ceramic substrate. These analyses were carried on both metallographically prepared 1-2-3/Ag-contact/solder alloy/metal conductor (lead-wire) samples and on the samples that were fractured by pulling off the soldered on lead-wires. Mechanical testing of metallized samples before and after thermal cycling has been performed to establish the strength of the developed joint between the HTSC and metal.

Environmental Stability - Degradation of Metallized Samples

The environmental stability was investigated by Optical Microscopy, SEM and Surface Analysis examination of metallized samples before and after exposure to laboratory environment, water at room temperature, controlled atmosphere and thermal cycling tests

3.0 RESULTS AND DISCUSSIONS

3.1 Metallographic Characterization of Metallized Samples

3.1.1 Microstructure of 1-2-3 Superconductor

Figure 7 shows a typical cross section of the 1-2-3 superconductor sample fabricated in our laboratory. The fabricated ceramic is a relatively dense material consisting of well faceted grains of maximum 20μ in diameter; some twin boundaries are also visible on this micrograph. The detailed grain structure of this material was characterized by SEM examination of the fractured samples. A typical micrograph is shown in Figure 8. This examination confirmed the results of optical microscopy examination; the ceramic was compact and consisted of randomly oriented grains that fractured in both intergranular and transgranular modes. The grains that fractured in the intergranular mode are well faceted (location A on Figure 8) with pores at triple-point grain boundaries. The transgranular fracture is shows entrapped pores (pores within the grains) as seen at location B on the same micrograph. Further examination of these features can provide valuable information about the effect of thermal history and processing on the superconducting material microstructure.

3.1.2 1-2-3/Silver Interface

After the visual observation (Figure 9) of the superconductor surface metallized by different

techniques, the cross sections of these samples were examined by optical microscopy. Figure 10 shows typical micrographs of samples that were metallized by the new, "in-house" developed technique (Figure 10A), fabricated and metallized by CPS Superconductor Corporation in the USA (Figure 10B) and metallized by METCO flame spray technique (Figure 10C). These micrographs indicate that the silver contacts produced by depositing Ag-epoxy through a silk-screen mask ("in-house" contacts) were compact and adhered perfectly to the ceramic substrate as a result of the silver penetration into the ceramic material. The contacts on samples from CPS Superconductor Corporation were nonuniform and porous. The silver layer deposited by flame spray technique penetrated well into the ceramic but the contact was porous and discontinuous. Therefore, only the contacts deposited by the "in-house" technique were used for further evaluation and development. The micrograph in Figure 11 shows the results of SEM/EDX (Energy Dispersive X-Ray) examination. There are no observable gaps at any location between the silver layer and the 1-2-3 sample to indicate a physical separation and therefore the lack of contact. X-Ray mapping of the cross sectioned sample indicated that the contact layer is coating uniformly the surface of the superconductor sample.

3.1.3 Integrity of "In-House" Deposited Ag-Contacts

Optical microscopy was used to examine the adherence of silver contact to both, the ceramic superconductor and the solder alloy. The micrographs in Figure 12 show the typical cross sections through the 1-2-3/Ag-contact deposited through a silk-screen mask/Sn, Pb solder/lead-wire sample. These confirm that the "in-house" deposition technique produced silver contacts that exhibit an excellent adherence to the ceramic substrate (Figure 12A). Furthermore, the micrograph in figure 12B shows an unbroken interface between the silver contact and solder (63/37 Sn/Pb alloy) layers indicating that this solder alloy exhibits an excellent wetting of the contact surface.

3.2 Chemical Stability of 1-2-3/Ag-Contact/Solder/Lead-Wire Sample

To establish the effect of contact and solder materials on the stability of metallized 1-2-3 samples, surface analysis techniques have been used to examine the elemental composition and distribution in the 1-2-3 compound before and after their metallization and lead-wire attachment. Therefore, the surfaces of freshly fabricated superconductor, superconductor underneath the Ag-contact and metallographically prepared cross sections have been analyzed by SIMS and AES. Both, these techniques indicate that the silver contact penetrated deep into the ceramic substrate. The Auger silver scan line shows a diffuse profile of Ag-contact/1-2-3 interface because silver diffusion into the ceramic substrate (Figure 13) during metallization process. However, the oxygen line scan (Figure 14) displays a sharp interface between the silver and the 1-2-3 sample indicating that there was no oxygen diffusion from the superconductor into the contact layer. SIMS imaging (Figure 15) and Auger mapping (Figure 16) of the cross sectioned 1-2-3/Ag-contact/Pb, Sn solder/lead-wire sample show an insignificant diffusion of solder components, Sn and Pb, into the contact layer. These observations prove that there was no interaction between the ceramic material and the solder alloy. The AES analysis indicates that both, the 1-2-3 surface (Figure 17A) and the fracture surface that resulted by pulling the lead-wire from the 1-2-3 sample (Figure 17B) indicates have similar elemental composition. This finding confirms that the "in-house" technique produced a contact layer which acted as an efficient barrier against diffusion of solder alloy components into the ceramic 1-2-3 sample.

3.3 Electrical Properties of Metallized Superconductor Sample

Considerable amount of information is available in open literature concerning the effects of processing parameters and metallurgical properties of HTSC materials on their superconductive properties/4,5,17,18/. To obtain reliable and characteristic values of electrical properties of metallized 1-2-3 samples, in this work the following factors were recognized and addressed :

- homogeneity of the investigated 1-2-3 samples as related to their microstructure and composition,
- surface preparation of superconductor sample before metallization,
- sample storage before and in between the tests,
- sample configuration (size and shape, contact geometry, distance between the voltage and current electrodes),
- proper selection of measurement conditions (material and size of sample holder, method of attaching the lead wires to the metallized sample),
- proper choice of experimental conditions for temperature measurement and type of thermocouple,
- adequate electrical measurement instrumentation (electric power source, noise level and sensitivity of voltmeters),
- establishment of an accurate system of defining the critical properties of superconductors sample and contact resistivity of metallized sample.

3.3.1 Contact Resistivity

To assess the electrical performance of contacts that were deposited by different techniques, and/or exposed to different experimental conditions, the contact resistivity was measured as described in the previous section. Tables 3 and 4 present typical results of these measurements.

Reports in the technical literature describe several silver deposition techniques/9,12-15/ producing contacts that exhibit very low contact resistivity as shown in Table 3. In this work we have made several attempts to reproduce some of these contacts experimentally. For example the sample metallized by plasma arc spray at Perkin Elmer laboratory produced a contact that exhibited very low contact resistivity (5×10^{-8} $\Omega.cm^2$). Unfortunately, the sample showed very poor mechanical properties; on most of the tested samples the contact separated from the sample during soldering process. Only after these samples were heat treated, we were able to solder on the lead-wires, and measure the contact resistivity. Similar results were obtained with the samples that were metallized by thermal evaporation. The contact exhibited very poor adherence to the 1-2-3 samples. Since the samples that were metallized by the "in-house" technique exhibited good mechanical properties and very low electrical contact resistivity, that compares well to that reported in literature, only this metallizing technique was used to prepare contacts for further testing.

testing.

Furthermore, the results in Table 4 indicate that the "in-house" metallizing technique produced contacts with lower resistivity than those deposited by simple painting or stamping the Ag-epoxy slurry. It is speculated that the masking method used in this investigation facilitates the deposition of a uniformly thick silver layer. It was also established that the contact resistivity depends on the type of solder material used to attach the lead-wires. Higher electrical contact resistivity was measured with indium than with Sn/Pb solder alloys. Since indium has a high affinity for oxygen, it is assumed that indium solder alloys oxidized during soldering procedure, thus increasing the contact resistivity.

To further improve the contact performance, the preparation of the ceramic sample prior to metallization process, the post-metallization heat treatment and the method to attach the lead-wire were optimized. Practically, no changes were detected on samples that had different surface roughness as a result of abrading them with different silicon carbide papers prior to metallization. When Ag-epoxy slurry was used to attach the silver lead-wires, it was possible to position them very close to the contact layer. This resulted in very low contact resistivity, varying between 3.5×10^{-9} and $1 \times 10^{-9} \Omega.cm^2$. These values are comparable with the best data reported in the technical literature/14/. However, for practical reasons only the soldering procedure was used to join the lead-wires to the metallized samples used for subsequent assessments.

3.3.2 Critical Properties of 1-2-3 Samples

Critical Temperature

The experimental methodology used to define the critical temperature of 1-2-3 samples was chosen so that our results could be compared with the data from technical literature. The details of this procedure are summarized in Appendix B.

Figure 18 illustrates the typical resistivity-temperature curve for the 1-2-3 superconductor samples prepared in OHRD's laboratory. This graph indicates that the performance of our superconductor samples compares well with those prepared by other laboratories outside Ontario Hydro. In general, the typical values for T_c onset ranged from 89 to 92 K depending on the batch of the samples, metallizing technique and storage conditions. The 1-2-3 samples purchased from the Superconductor Corporation in the USA exhibited lower T_c than our samples. Insignificant changes of T_c with the length of storage time were detected when the samples were not stored in a desiccator. Work that was carried out to establish the effect of laboratory environment on T_c values is now completed and will be reported separately.

Figure 19 shows the influence of the test current on T_c measurements. This graph indicates that when the test current was increased from 0.125 to 1A the value of the zero resistance in the resistance-temperature curve shifted toward the low temperature side reflecting the dependency of the critical temperature on the current. It is believed that Joule heat generated at the contacts increases the temperature of the sample. To eliminate this heating effect, low test current, 30 mA, was used to measure the T_c.

Critical Current Density

Critical current measurement could be used as a scientific tool for characterization of both, the superconductive properties of the bulk ceramic sample and electrical performance of HTSC/metal contact. Since the current can be transported across the different superconductor paths within the volume of the sample, the value of critical current density reflects the amount, the quality and homogeneity of the superconductive phase present within the ceramic sample. Therefore both, the material properties of the superconductor (microstructure, and phase and elemental microcomposition) and the contact configuration and stability have to be considered when critical current density of different samples is assessed/18/. Depending on the method that was used to deposit the contact and the type of soldering technique and alloys, the contact resistivity can exhibit different values and therefore, different amount of heating will be generated underneath the contact layers. Higher contact resistivity generates more heat and therefore, will produce inaccurate values for $J_{c\eta}$ as both current and temperature contribute to destruction of the superconductivity. Alternately, depending on the type of contact material, metal oxides can form at the contacts, or the current distribution may become uneven producing inaccurate J_c measurements.

The critical current density of 1-2-3 samples was measured by the technique described in the previous section. Figure 20 illustrates a typical V-I curve for 1-2-3 sample established by the four-point method. The critical current density determined from this curve was 44 A/cm^2. The values of Jc measured for different batches of samples ranged from 1.9 to 54.5 A/cm^2. Microscopical observation of the sample that exhibited only 1.9 A/cm^2 indicated presence of microcracks in the material underneath the silver contact layer. It is assumed that this low value of J_c is a result of the poor contact between the superconductor and silver layer. Therefore, the loss of superconductive properties occurred because of both, local increase in temperature and current density. The factors were found to influence the values of J_c are listed in Table 5. However, no attempts were made to improve critical density of our samples by modifying the fabrication technique, since this was beyond the scope of the present program.

3.4 Mechanical Stability of Metallized Samples (Contact Adherence)

To test the mechanical adherence of the investigated contacts, 1-2-3 sample/Ag-contact/solder lead-wire, a simple mechanical test was performed. The lead-wires were pulled in tension until they were detached from the system. These tests showed that the samples involving contacts deposited by the "in-house" metallizing technique invariably failed by fracture within the 1-2-3 material. This indicates that the joint developed between the silver contact and the superconductor was stronger than the 1-2-3 material. On the other samples that contained contacts deposited by different techniques, the mechanical stability of the contacts was so poor that in the most cases the silver layer was removed during the soldering procedure. Optical microscopy and SEM analysis confirmed the excellent contact achieved on the "in-house" metallized samples, since no physical gaps were observed between the ceramic materials and the silver layer and between the solder material and the silver layer (See Figure 12). Tension, shear and bending tests have been designed and performed to quantify the mechanical properties of investigated contacts and the results of these tests are reported separately/19/. These tests performed before and after the thermal cycling proved that the "in-house deposited contacts have adequate tensile and shear strengths.

3.5 Environmental Stability (Degradation of Metallized Samples)

To assess the degradation of metallized samples under different environmental conditions, the following tests have been carried out:

- exposure to laboratory environment,
- water immersion tests,
- tests under controlled atmosphere (100% humidity and $^{13}CO_2$)
- thermal cycling tests

Metallographic, chemical, electrical and gravimetric examination of the metallized samples before and after their exposure has been performed to establish the extent of their degradation. However, in this section of the report only the major findings are reviewed. The detailed results of the tests carried under different environmental conditions are reported separately/20,21/.

3.5.1 Laboratory Environment

The results of sample analyses showed that the 1-2-3 samples were attacked only superficially when exposed in the laboratory environment for periods of time up to six months. The microstructure of the bulk ceramic was unchanged (Figure 21A) and only an insignificant increase of the samples' weight was observed after the six month exposure tests (Table 6). Only a thin layer of new products resulting from the degradation of the 1-2-3 material was observed on the exposed surface (Figure 21B). As a result only the room temperature resistance increased while the other electrical properties were practically unaffected.

3.5.2 Water Immersion Tests

SEM examination of metallized 1-2-3 sample removed from water immersion tests (24-hours exposure) showed that the microstructure of the ceramic material was dramatically affected. The micrographs given in Figures 22A and B indicate that a new needle-like phase was formed at the grain boundaries of the ceramic. X-Ray diffraction of exposed sample indicated that the new compound was $BaCO_3$. This reaction with water took place on the surface, and within the volume of the sample away from the contacts. The microstructure of the ceramic underneath the contact was practically unchanged (Figure 22C). This indicates that the contact layer is compact and constitutes a protective barrier against environmental attack. The electrical tests showed that the T_c, J_c and contact resistivity of metallized 1-2-3 samples deteriorated as a result of sample immersion in the water.

3.5.3 Controlled Atmosphere

To study the contribution of atmospheric water (humidity) and carbon dioxide on the degradation mechanism of metallized 1-2-3 samples and the role played by the residual carbon, that is present in the superconductor samples as a result of fabrication procedure, experiments have been carried out in controlled atmosphere containing 100% humidity and CO_2 enriched in ^{13}C. The results of SEM examination of exposed samples showed that they contained the needle-like $BaCO_3$ phase (Figure 23). The SIMS analysis (Figure 24) detected both ^{13}C and ^{12}C in the degraded samples. This indicates that carbon dioxide originating from both, atmosphere and residual carbon, plays a role in the degradation process of 1-2-3 materials.

3.5.4 Thermal Cyclic Tests

To elucidate the effect of thermal stresses and water that condensate when the temperature changes from that of liquid nitrogen to that of the ambient environment, up to 50 thermal cycles were performed. Some of the sample were mildly heated after immersion in the liquid nitrogen prior to ambient environment exposure, to prevent the water condensation. Wet thermal cycling tests were also performed without heating the sample, to allow the atmospheric water (humidity) to condense on the sample surfaces. Electrical properties of the metallized samples were measured before and after a number of cycling tests was completed. The results of these measurements indicate that the interaction of condensed water with the microstructure of the ceramic material plays a major role in the degradation mechanism.

Therefore, the experimental tests carried out under different environmental conditions demonstrated conclusively that the silver contact that was deposited by the technique developed in our laboratory was unaffected by the environmental attack. However, the ceramic superconductor deteriorated as a result of its interaction with condensed water and carbon dioxide. Further work should be carried out to formulate procedures to protect the superconductor material used in any electrical device, against the environmental exposure to water condensation.

4.0 SUMMARY OF THE ACHIEVED RESULTS

The results of this work could be summarized as follows:

- A new technique to join a HTSC with a conventional metallic conductor was developed for testing. This technique consists of metallizing the ceramic 1-2-3 superconductor with silver and soldering the metallized sample to the metallic conductor.

- A reliable technique was developed to fabricate dense 1-2-3 samples required for metallizing.

- Five techniques to deposit metals on ceramic substrate were tested. Based on the results of these tests a metallizing technique was developed in our laboratory to produce reproducible and reliable contacts. This technique consists of pushing Ag-epoxy slurry through silk-screen or stencil-type mask depending on the slurry consistency and required thickness of the contact on the surface of the superconductor ceramic. The deposited slurry is then cured, sintered and annealed under specific conditions of temperature and environment determined in this work.

- Metallographical, electrical and mechanical tests were carried out to assess the performance of the developed contacts. These tests indicated that the new metallizing technique produced reproducible and reliable contacts. The deposited silver contacts are characterized by an excellent adherence to the 1-2-3 superconductor substrate, an exceptionally low electrical contact resistivity ranging from 10^{-8} to $10^{-9}\Omega.cm^2$ and environmental stability. In tension the joint between the 1-2-3 superconductor and deposited silver was stronger than the superconductor itself.

- Laboratory tests performed under controlled environmental conditions proved that the 1-2-3 superconductor is very susceptible to attack by condensed water and carbon dioxide. Therefore, methods to protect the surface of the superconductor component against the environmental attack should be developed to ensure the reliability of any electrical component that may be designed in the future.

Approved by:

N. Anyas-Weiss
Manager
Divisional Projects Department

Reviewed by:

F.Y. Chu
Section Head
Science Section
Electrical Research Department

Submitted by:

A.V. Manolescu
Engineer - Corrosion
Science Section
Electrical Research Department

P. Mayer
Senior Metallurgist
Materials Technology Section
Metallurgical Reserach Department

S. Krishnasamy
Unit Head
Applied Mechanics Section
Mechanical Research Department

E. Di Blasio
Technician
Mechanical Testing and Development Section
Mechanical Research Department

M. Eygenraam
Intermediate Technician
Science Section
Electrical Research Department

TABLE 1

METALLIZING TECHNIQUES

Type of Techniques	Technique Description	Research Laboratory
Ag-Epoxy	Painting Ag-epoxy (Epo-Tek H2OS) on ceramic samples and annealing at 900 C in flowing O_2	OHRD
Thermal Deposition	Depositioning Ag onto the ceramic pellets through shadow masks by thermal evaporation in vacuum.	OHRD, Queen's University
Sputtering	Sputter-etching the ceramic sample and sputtering the Ag in vacuum; post-deposition annealing in flowing O_2 at 500-600 C.	OHRD
Pressing/Sintering	Pressing Ag-wire and 1-2-3 powder using a "in-house" designed die; post-deposition sintering at 950°C in flowing oxygen	OHRD
Thermal spray	**Flame Spray** Deposition of Ag-wire using a oxy-acethylene gun and annealing at 900°C.	METCO (CANADA)
	Plasma Arc Spray Powdered Silver (-270/+325 mesh) was plasma sprayed with a gun onto the samples's masked surface.	PERKIN-ELMER (USA)

TABLE 2
SUMMARY OF METALLOGRAPHIC AND SURFACE ANALYSES

Analyzed location within the investigated samples	Type of Information	Type of Techniques
HTSC (1-2-3 Compound)	Porosity, Grain Structure Environmental effect on the grain structure of 1-2-3 sample	Optical Microscopy Scanning Electron Microscopy
HTSC/Ag Interface	Contact Adherence, Ag Penetration, Thickness of Ag-Layer, Ag-Diffusion Grain structure underneath the contact after environmental exposures	Optical Microscopy Scanning Electron Microscopy Energy Dispersive X-ray Analysis
HTSC/Ag/Solder/Lead-Wire	Ag-Diffusion; Solder Components Diffusion, Oxygen Depth Profile, HTSC Contamination	Scanning Electron Microscopy Auger Electron Spectroscopy Secondary Ion Mass Spectroscopy

TABLE 3
CONTACT RESISTIVITY OF METALLIZED HTSC

Type of Metallizing Technique	Contact Resistivity ($\Omega.cm^2$)	Comments
Melting Au*	5×10^{-7}	Good Adherence
Sputtering & Annealing*	6×10^{-10}	Adherence not reported Very small contact area
Thermal Evaporation*	4×10^{-8}	Adherence not reported
Pressing/Sintering*	1.6×10^{-12}	Adherence not reported Very small contact area
Plasma Arc Spray*	3×10^{-8}	Adherence not reported
Ag-Epoxy Deposition*	$<10^{-7}$	Adherence not reported
"In-House Developed" Ag-Epoxy deposition	1.5×10^{-8}	Very good Adherence and Stability
*Data reported in technical literature		

TABLE 4

CONTACT RESISTIVITY

Type of Contact	$R_{CONTACT}$ ($\Omega.cm^2$)
Ag-Epoxy (stamped)	$3.0 - 1.6 \times 10^{-7}$
Ag-Epoxy (silk-screen) using 63-37 Sn-Pb solder alloy	1.5×10^{-8}
Ag-Epoxy (silk-screen) using Indium containing solder	4.6×10^{-7}
Ag-Epoxy (sintered at 925°C; lead wires attached with Ag-Epoxy	$6.0 - 1.0 \times 10^{-9}$

TABLE 5

FACTORS AFFECTING THE CRITICAL CURRENT DENSITY

1.	Sample Quality (processing technique): - Microstructure - Microcomposition - Homogeneity
2.	Contact Performance
3.	Sample Storage
4.	Sample Design

TABLE 6

ENVIRONMENTAL DEGRADATION OF $YBa_2Cu_3O_{7-x}$

ENVIRONMENT CONDITIONS			WEIGHT GAIN (mg)*	REMARKS
Type of Environment	Exposure Time (Hours)	Temperature (°C)		
Laboratory Atmosphere	1080	RT	0.75	Mild, superficial attack. The material underneath the contact was not degraded. The sample surface was covered with a new product layer consisting of crystallites and amorphous cotton-like formation
Laboratory Atmosphere	2880	RT	1.00	
De-ionized Water	0.3	RT	9.00	Aggressive attack that initiated at the grain boundaries of the $YBa_2Cu_3O_{7-x}$. The new crystallites formed at the grain boundaries and spread across the ceramic grains. No degradation of the superconductor underneath the contact was detected. $BaCO_3$ and CuO phases were identified by x-rays diffraction analysis.
De-ionized Water	9	RT	10.00	
De-ionized Water	29	RT	15.00	
*All tested samples had the same exposed surface area.				

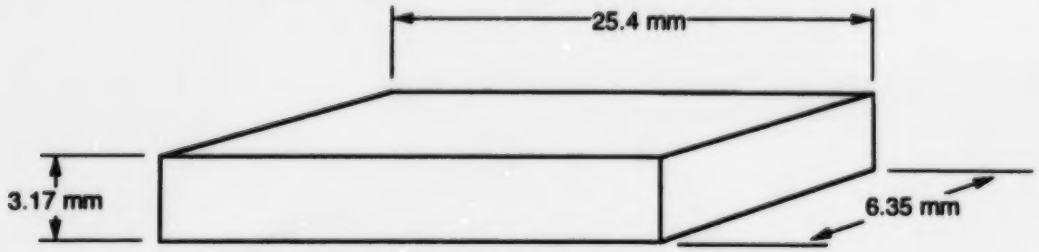


FIGURE 1

DIMENSIONS OF THE $YBa_2Cu_3O_{7-x}$ SAMPLE FABRICATED FOR TESTS IN THIS WORK

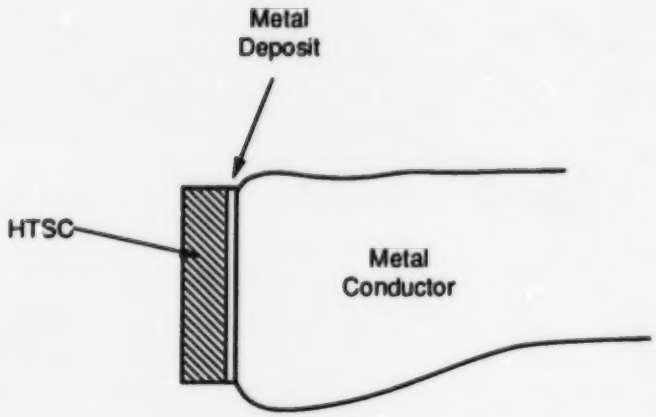


FIGURE 2

SCHEMATIC OF HTSC / METAL JOINT

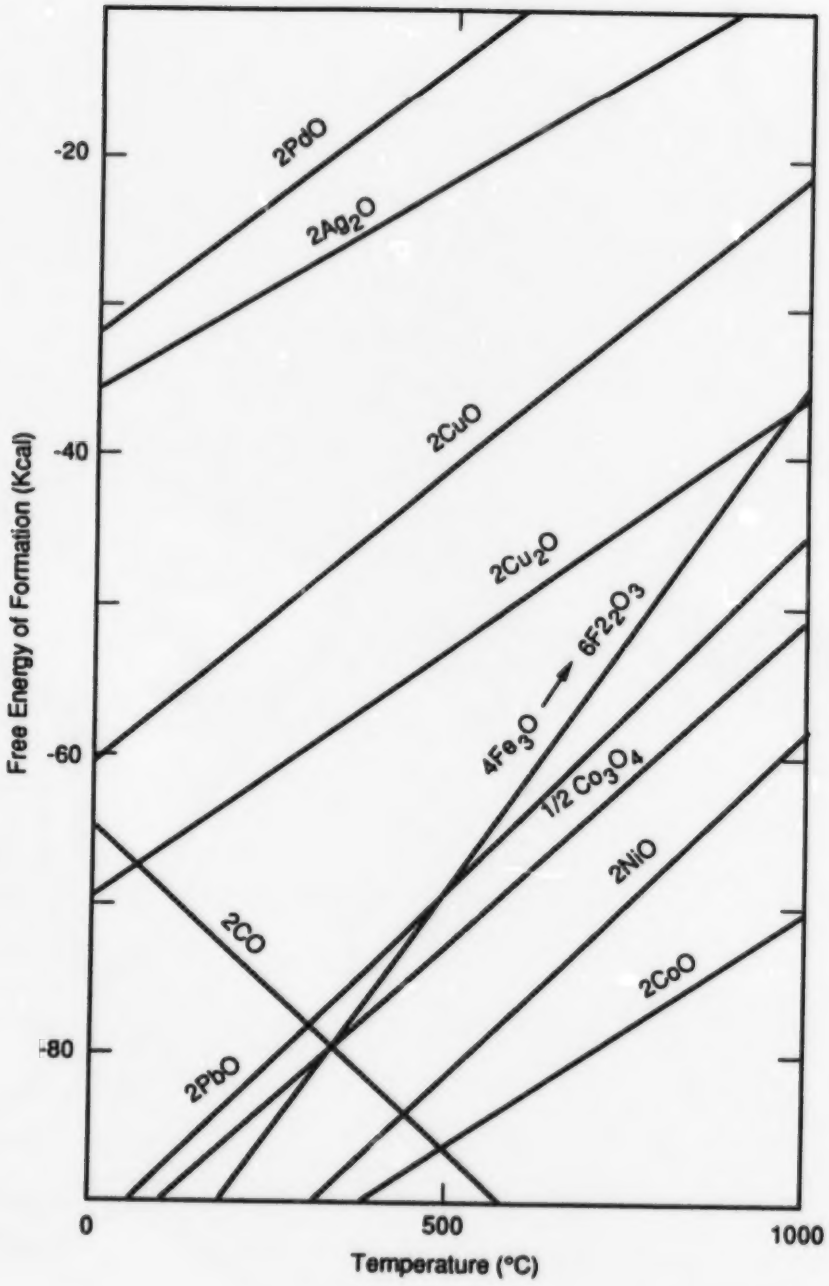


FIGURE 3

STANDARD FREE ENERGY OF FORMATION OF OXIDES INVOLVED IN THIS WORK

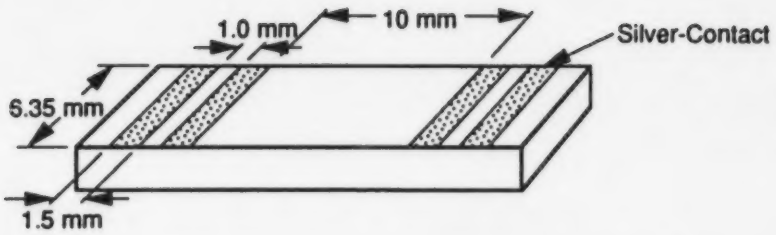


FIGURE 4

CONFIGURATION OF SILVER-CONTACTS USED FOR THIS INVESTIGATION

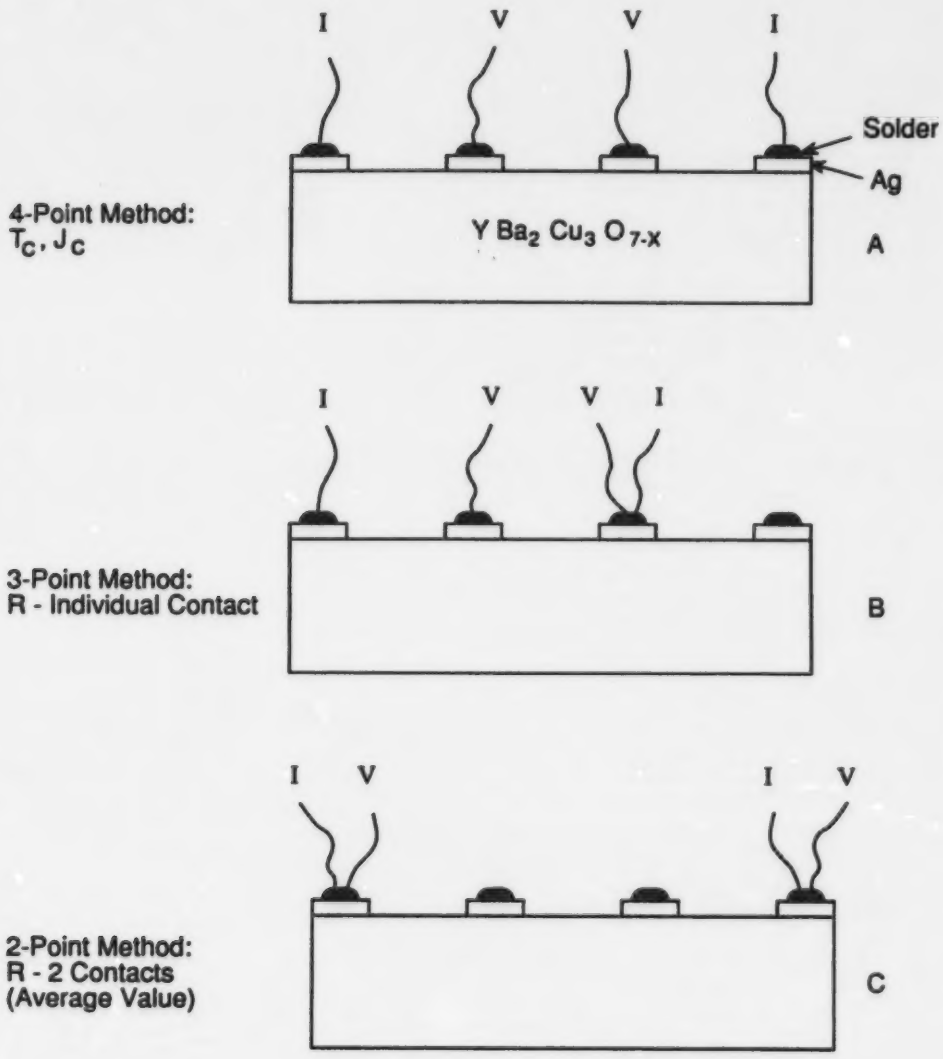
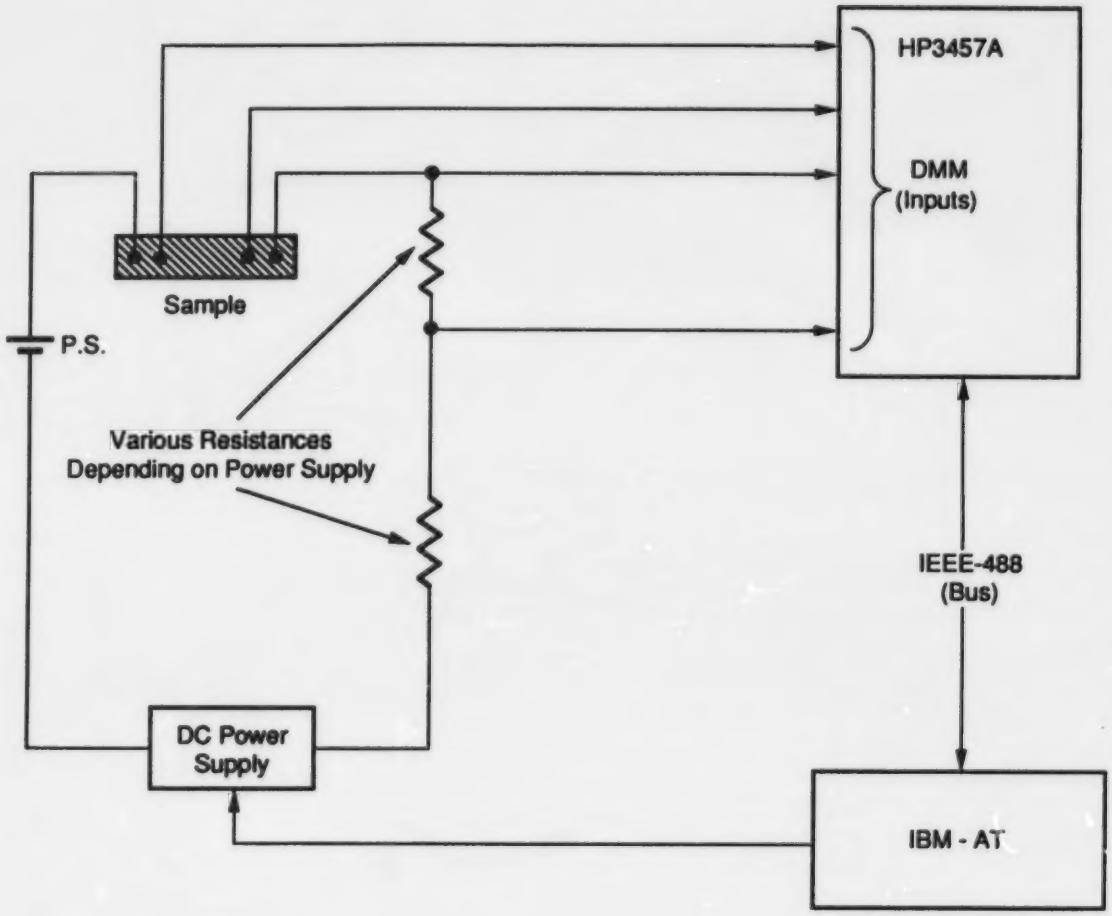


FIGURE 5

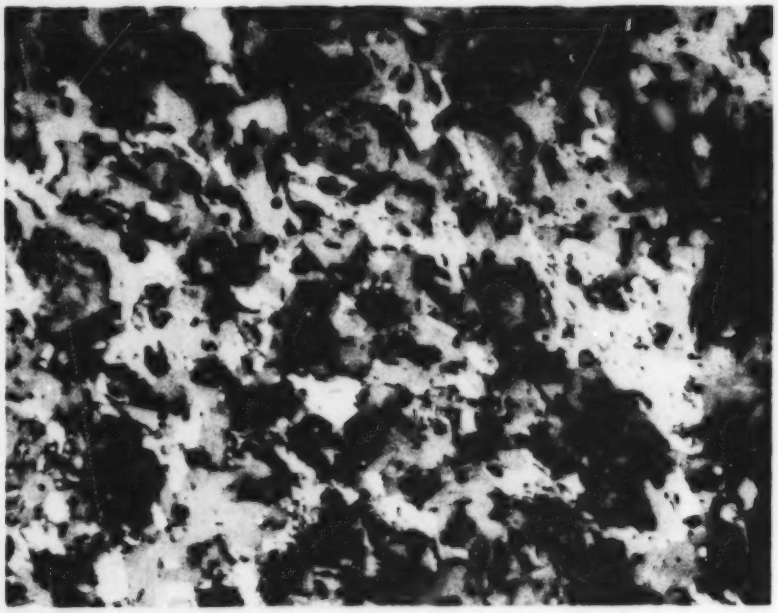
SAMPLE CONFIGURATIONS USED TO ASSESS THE ELECTRICAL PROPERTIES OF METALLIZED SAMPLES



Note: Thermocouple wires which contact the sample are also inputs to the DMM.

FIGURE 6

SCHEMATIC OF TEST SET-UP
USED FOR ELECTRICAL MEASUREMENTS



(x 400)

FIGURE 7

TYPICAL MICROGRAPH OF A CROSS-SECTIONED
$YBa_2Cu_3O_{7-x}$ SAMPLE UNDER POLARIZED LIGHT

(x 2000)

FIGURE 8

SEM MICROGRAPH OF FRACTURED
$YBa_2Cu_3O_{7-x}$ SAMPLE

91-52
184158-B23-RD

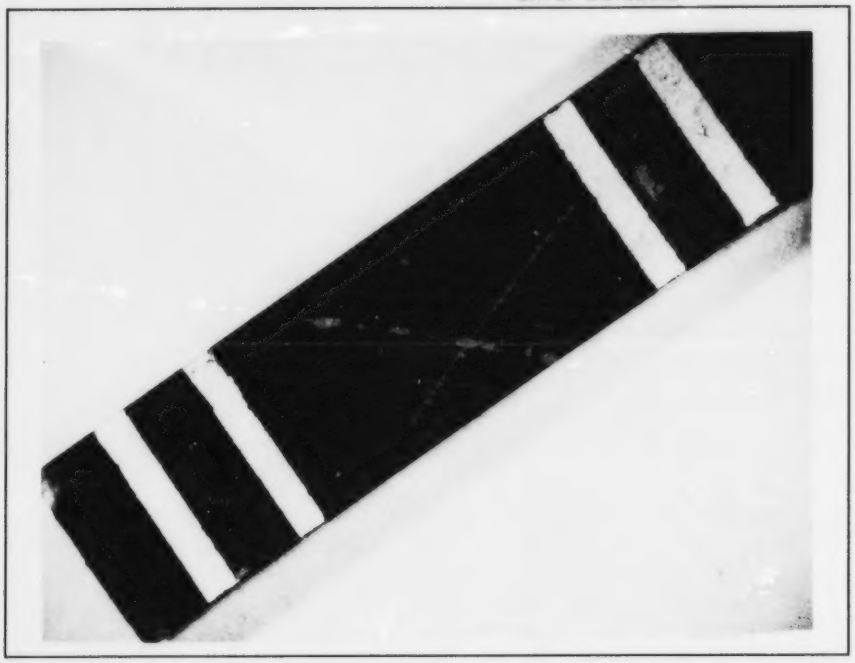
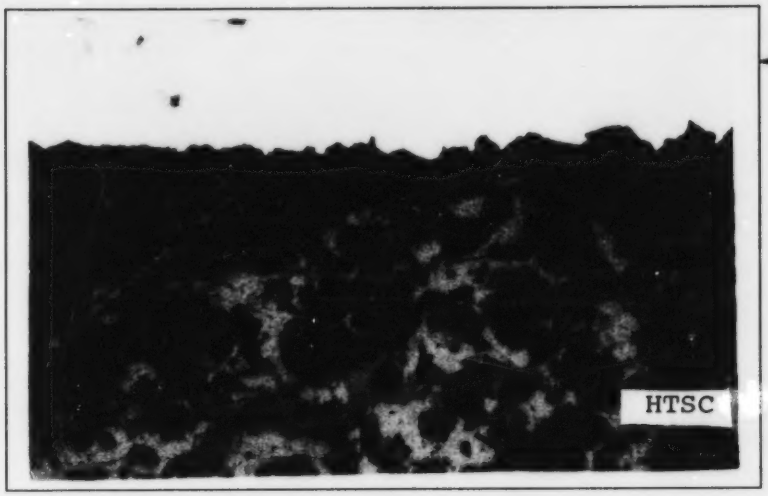


FIGURE 9

SURFACE VIEW OF METALLIZED $YBa_2Cu_3O_{7-x}$ SAMPLE (Ag-Epoxy Deposition)



Silver-Contact Layer

A

(x 400)

Silver-Contact Layer

B

(x 400)

Silver-Contact Layer

C

(x 600)

FIGURE 10

TYPICAL MICROGRAPHS OF METALLIZED SAMPLES

A - Sample Metallized Through a Silk-screen Mask (OHRD)
B - Sample Produced and Metallized by Superconductor Corporation (USA)
C - Sample Metallized by METCO Canada

91-52
184180-B23-RD

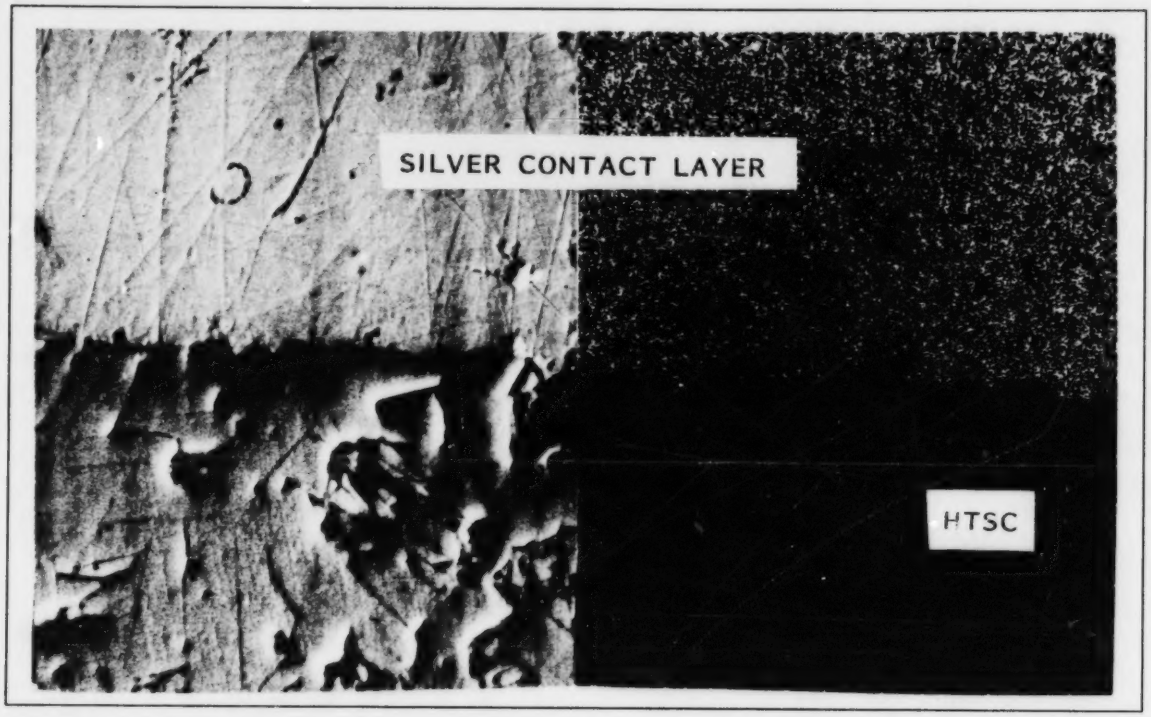
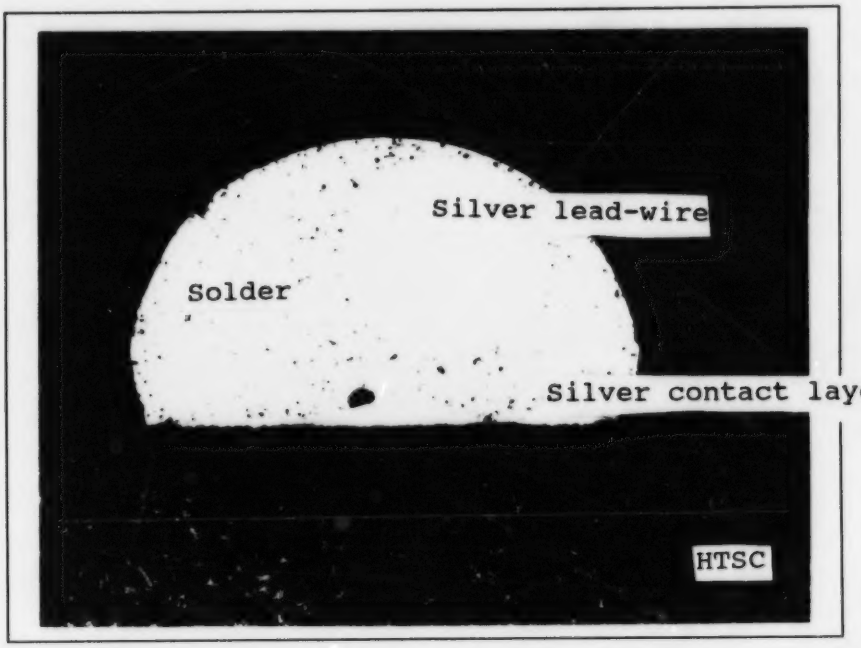


FIGURE 11

SEM EXAMINATION OF 1-2-3/Ag-CONTACT INTERFACE

A - SEM Micrograph
B - EDX Mapping for Ag



A

(x 50)

Solder

B

Ag-Contact

(x 600)

FIGURE 12

TYPICAL MICROGRAPHS OF 1-2-3
Ag-CONTACT / SOLDER ALLOY / LEAD-WIRE SAMPLE

A - Lower Magnification of Investigated Sample
B - Details of Solder/Ag-Contact Interface

91-52
184182-B23-RD

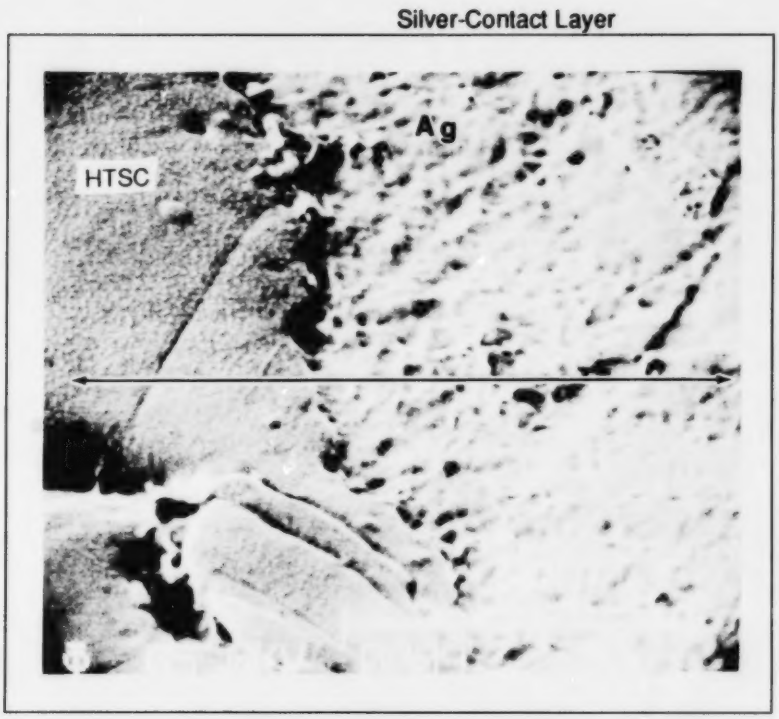


FIGURE 13

**AUGER SCANNING LINE FOR SILVER
ACROSS THE 1-2-3 / Ag - CONTACT INTERFACE**

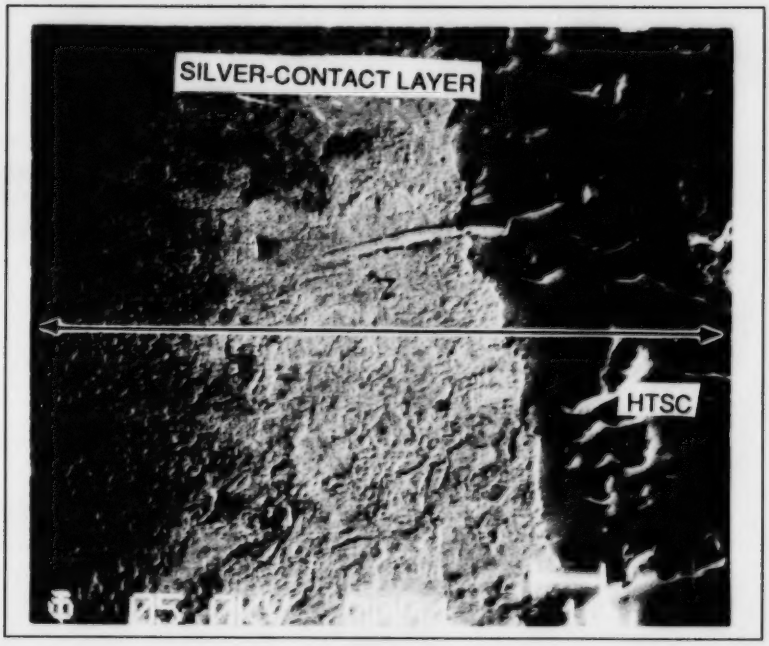
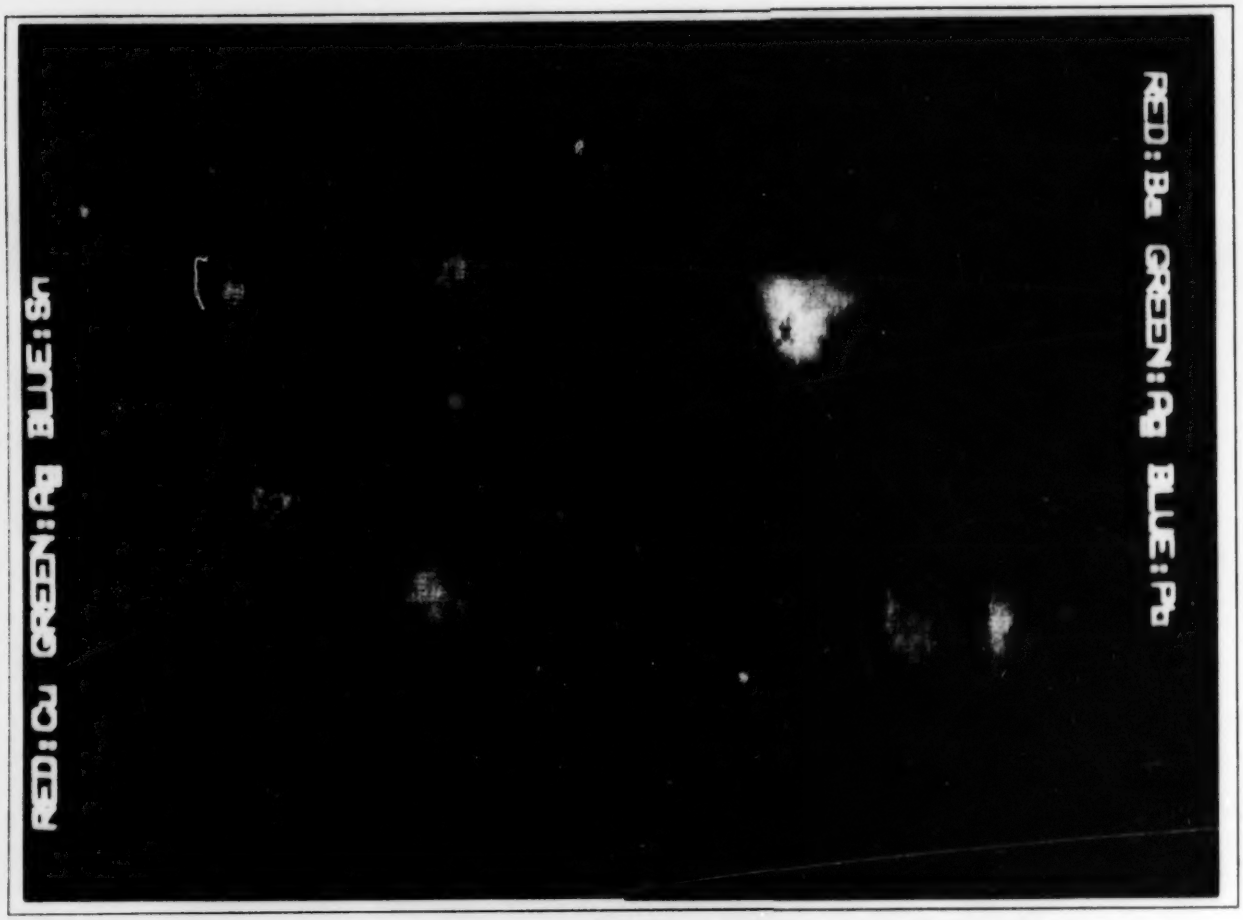


FIGURE 14

**AUGER SCANNING LINE FOR OXYGEN
ACROSS THE 1-2-3 / Ag - CONTACT INTERFACE**



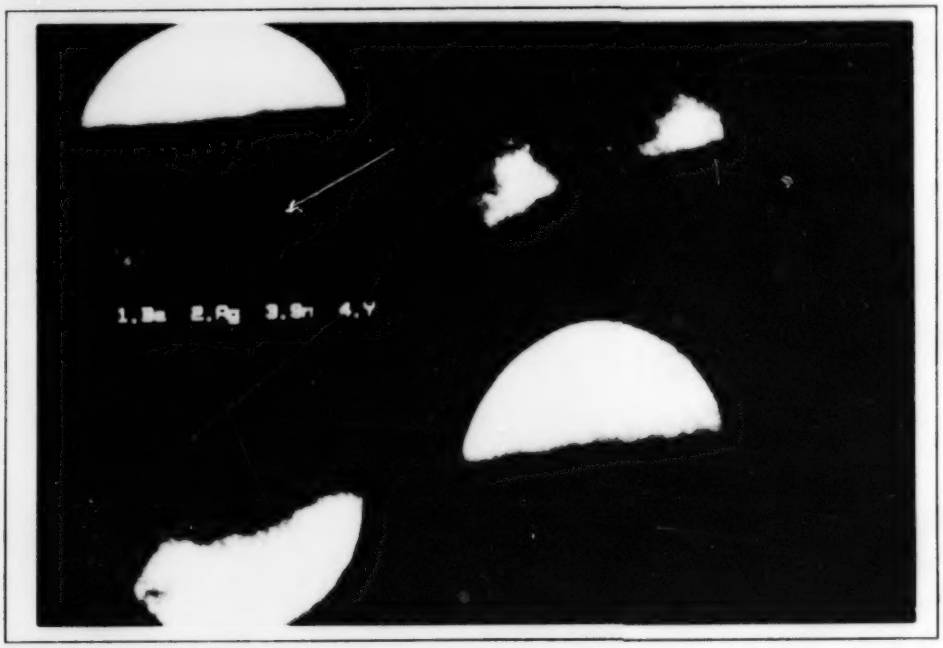


FIGURE 15

SIMS IMAGING OF 1-2-3 / Ag - CONTACT / Sn, Pb SOLDER / LEAD-WIRE SAMPLE

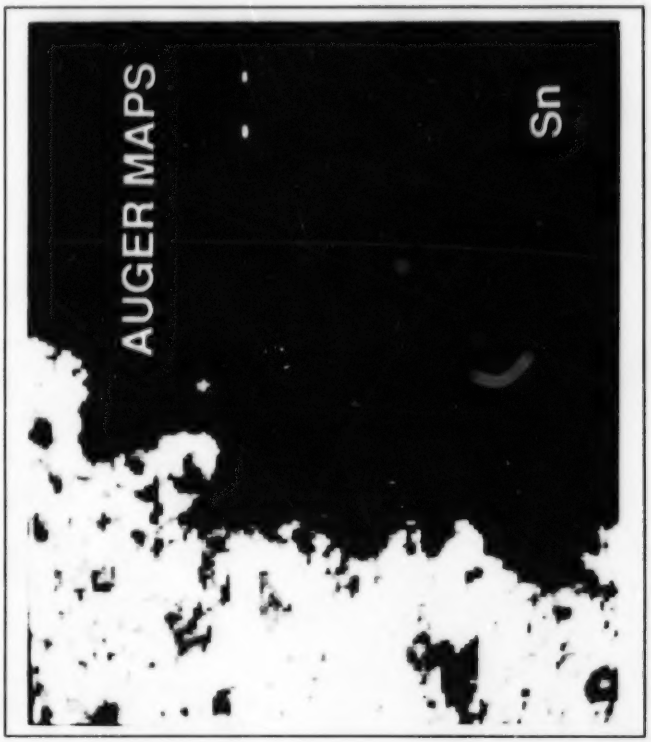


FIGURE 16

AUGER MAPPING OF 1-2-3 / Ag - CONTACT / Pb, Sn SOLDER/LEAD-WIRE SAMPLE

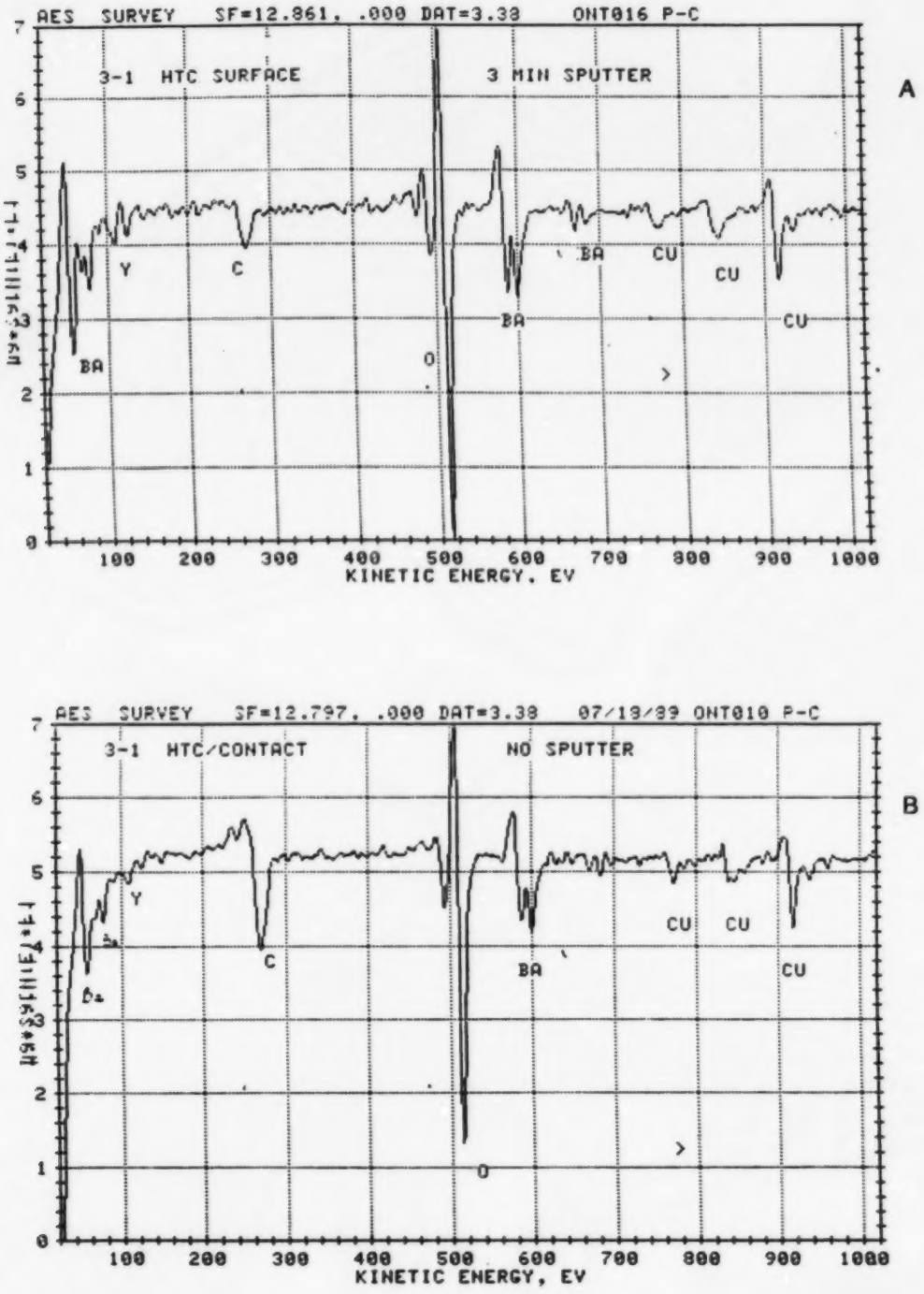


FIGURE 17

AES EXAMINATION OF 1-2-3 SAMPLE
A - AES Spectra of the AESC Sample on the Surface
B - Underneath the Removed Contact

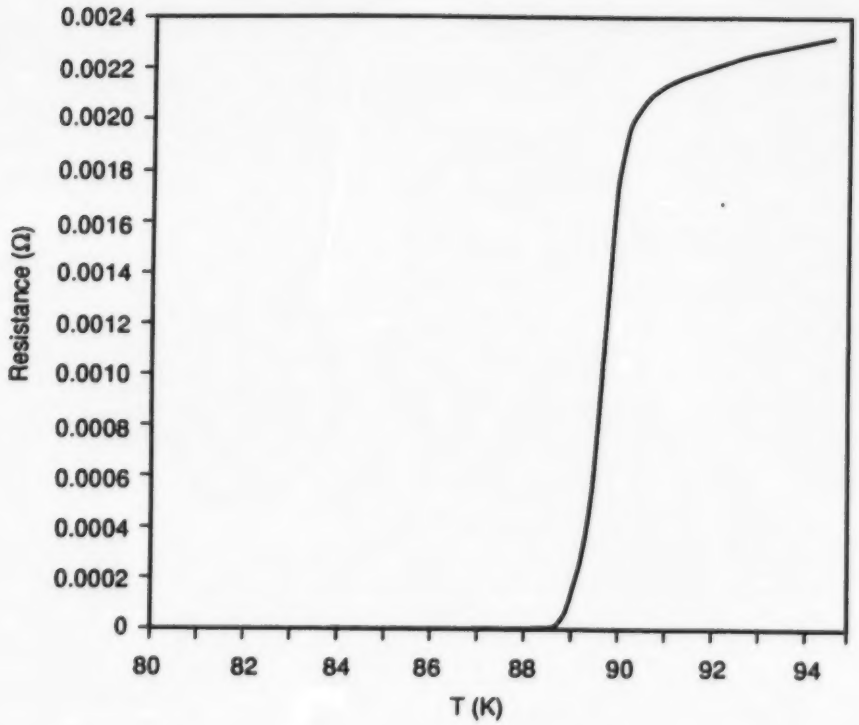


FIGURE 18

TYPICAL RESISTANCE VS. TEMPERATURE CURVE FOR 1-2-3 SAMPLES PREPARED AND METALLIZED AT OHRD'S LABORATORY

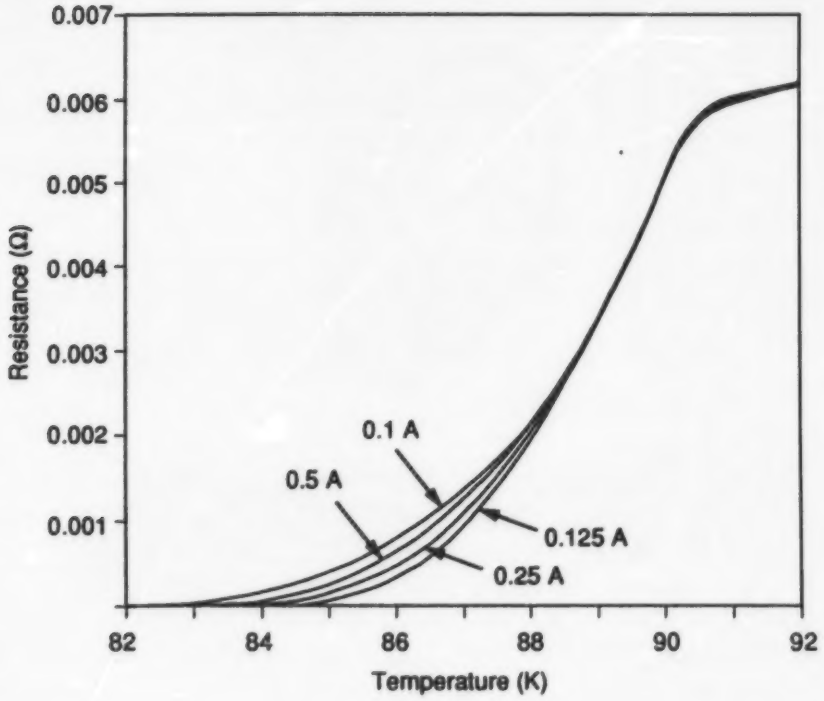


FIGURE 19

EFFECT OF TEST CURRENT ON T_c CURVE

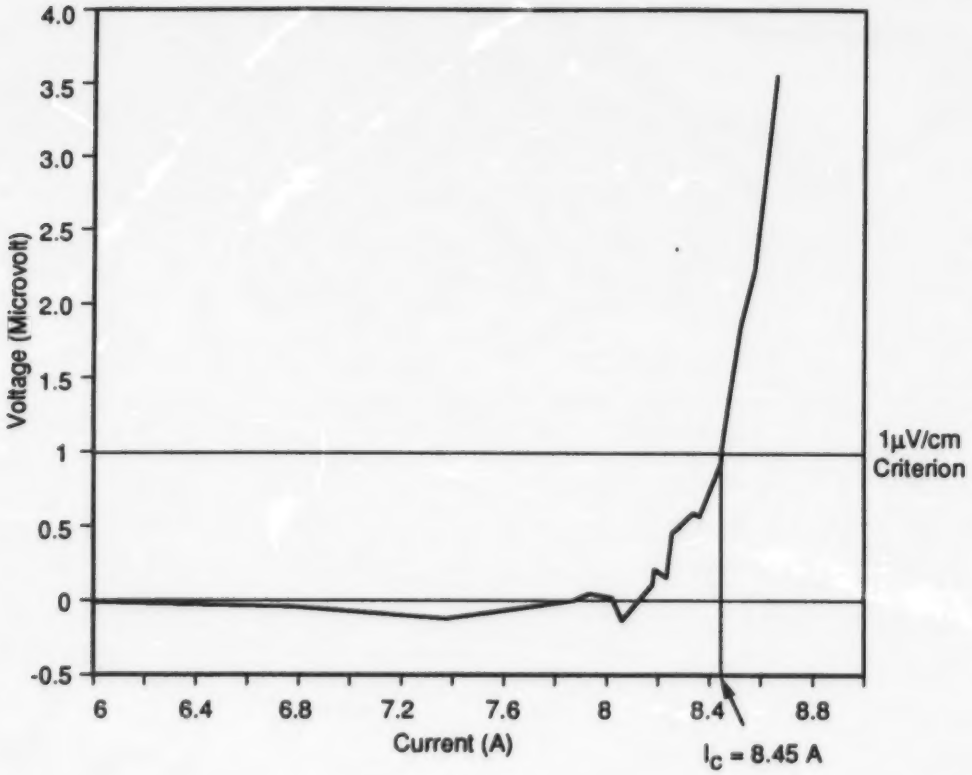
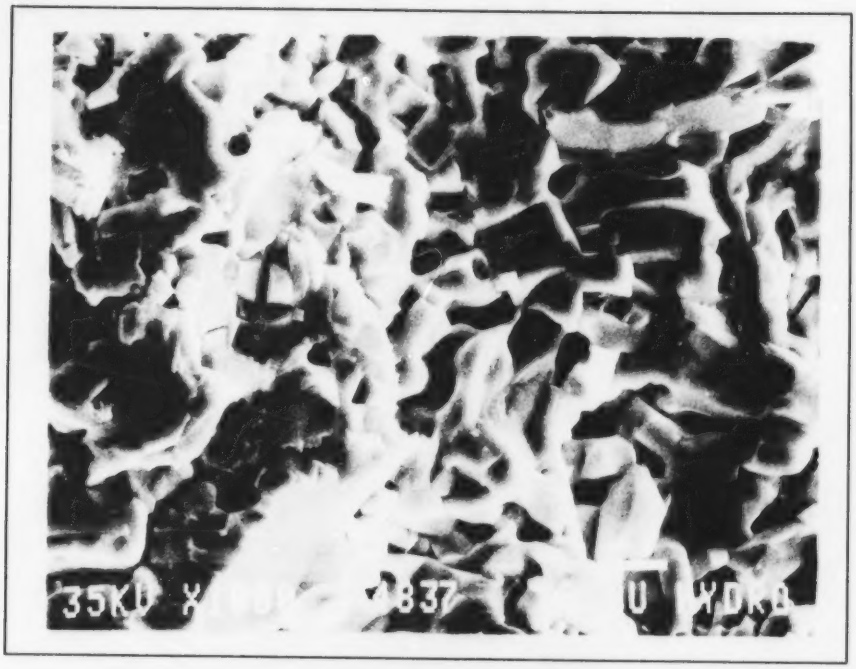
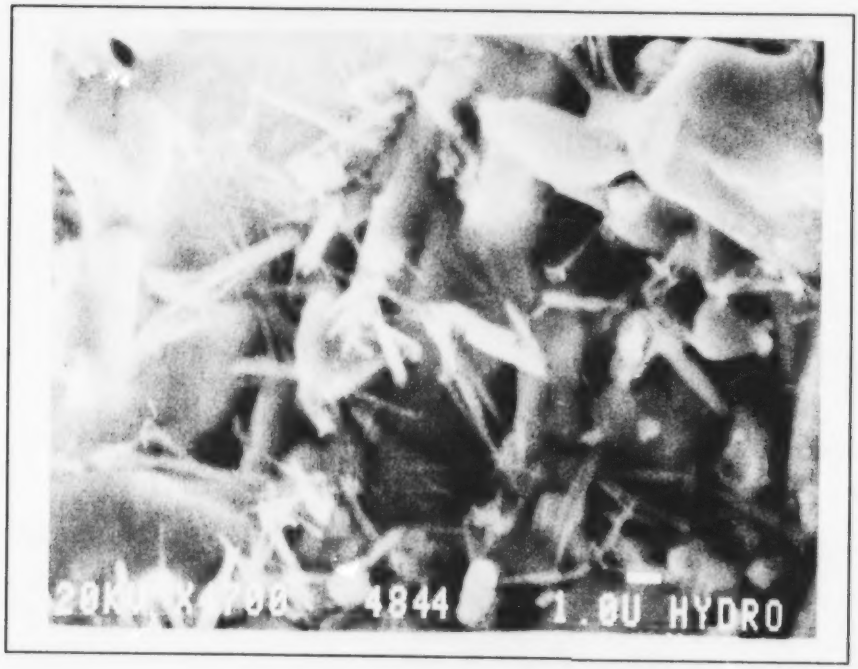


FIGURE 20

TYPICAL V-I CURVE USED TO EVALUATE THE CRITICAL CURRENT DENSITY METALLIZED 1-2-3 SAMPLES



A

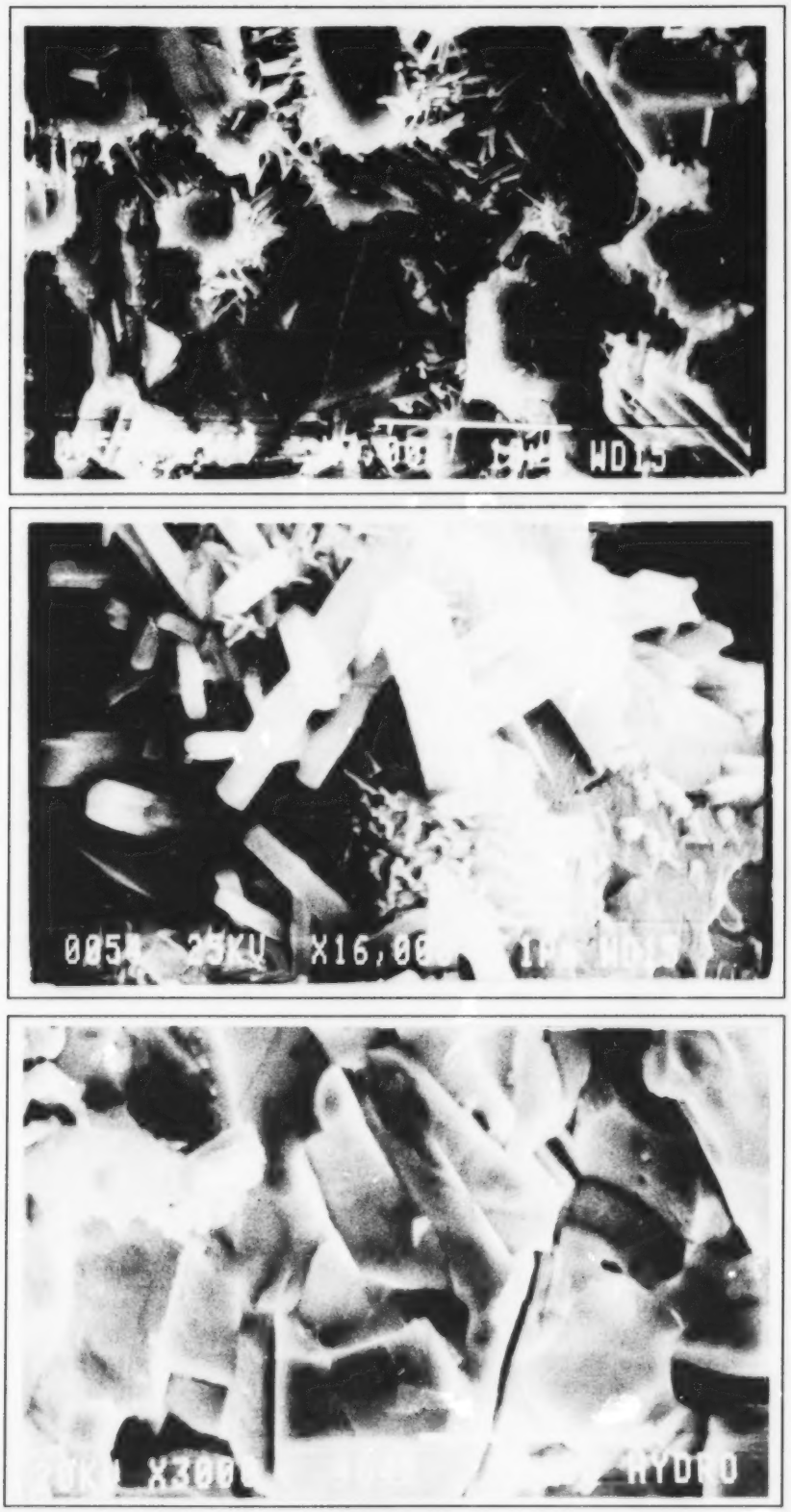


B

FIGURE 21

SEM MICROGRAPHS OF A SAMPLE EXPOSED TO LABORATORY ENVIRONMENT

A - Fracture Surface
B - Microstructure of the Exposed Surface



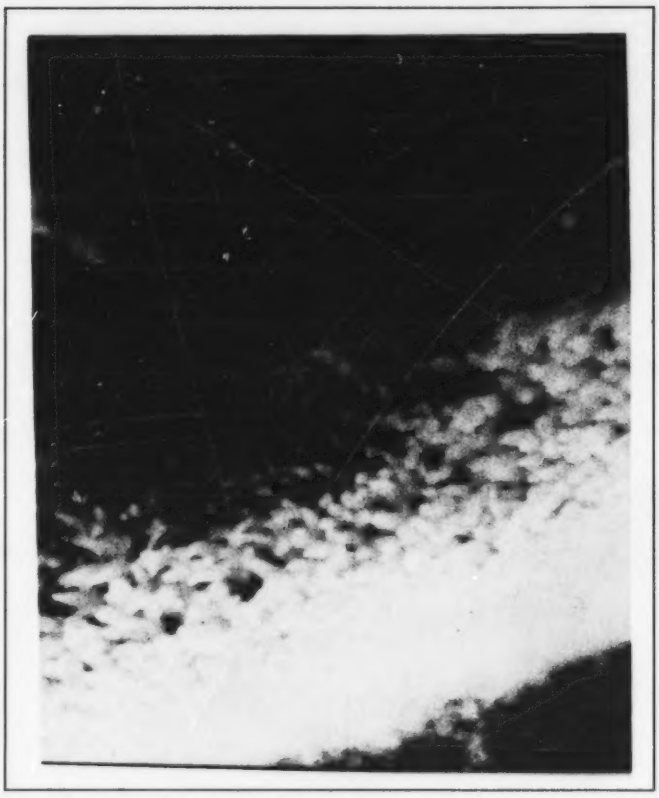
A

B

C

FIGURE 22
SEM MICROGRAPHS OF FRACTURED METALLIZED CERAMIC SHOWING ENVIRONMENTAL DEGRADATION

A. Microstructure of 1-2-3 Ceramic Immersed in Water for 24 hours
B. Same as Above. Details of New / Formed Needle-like Phase
C. Same as Above. Fractured Ceramic Underneath the Ag-Contact



(x 1.500)

FIGURE 23

SEM MICROGRAPH OF A METALLIZED SAMPLE EXPOSED TO CONTROLLED ENVIRONMENT (100% HUMIDITY AND ^{13}C)

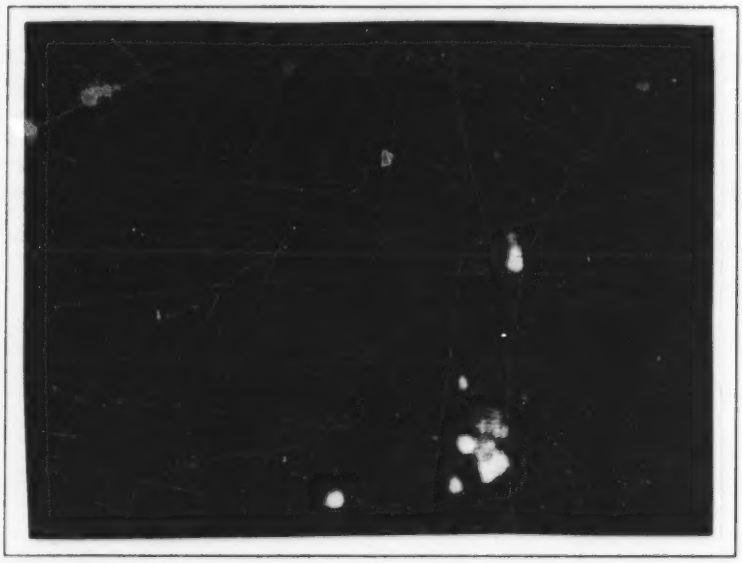


FIGURE 24

SIMS IMAGING OF A SAMPLE AFTER EXPOSURE TO CONTROLLED ENVIRONMENT (100% HUMIDITY AND $^{13}CO_2$)

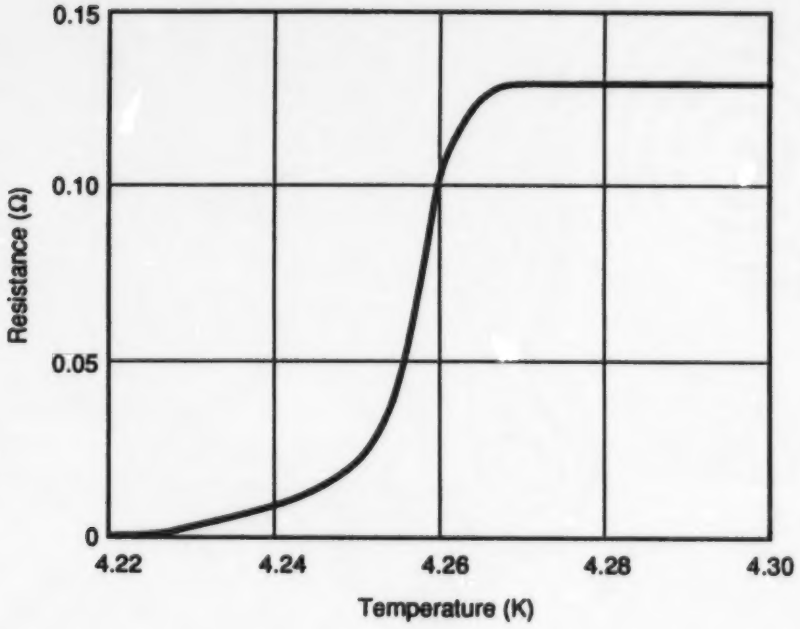


FIGURE A1

DEPENDENCE OF ELECTRICAL RESISTANCE OF MERCURY ON TEMPERATURE/2/

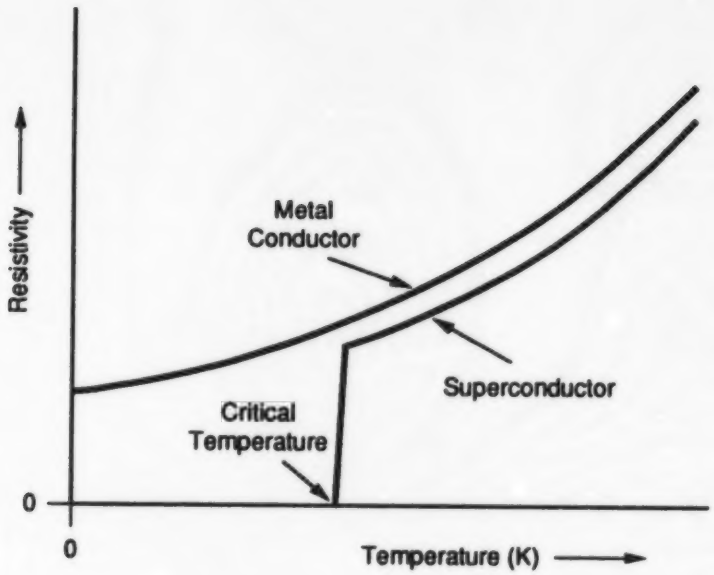


FIGURE A2

A GENERALIZED COMPARISON OF RESISTIVITY FOR NORMAL METALS AND SUPERCONDUCTORS AS A FUNCTION OF TEMPERATURE

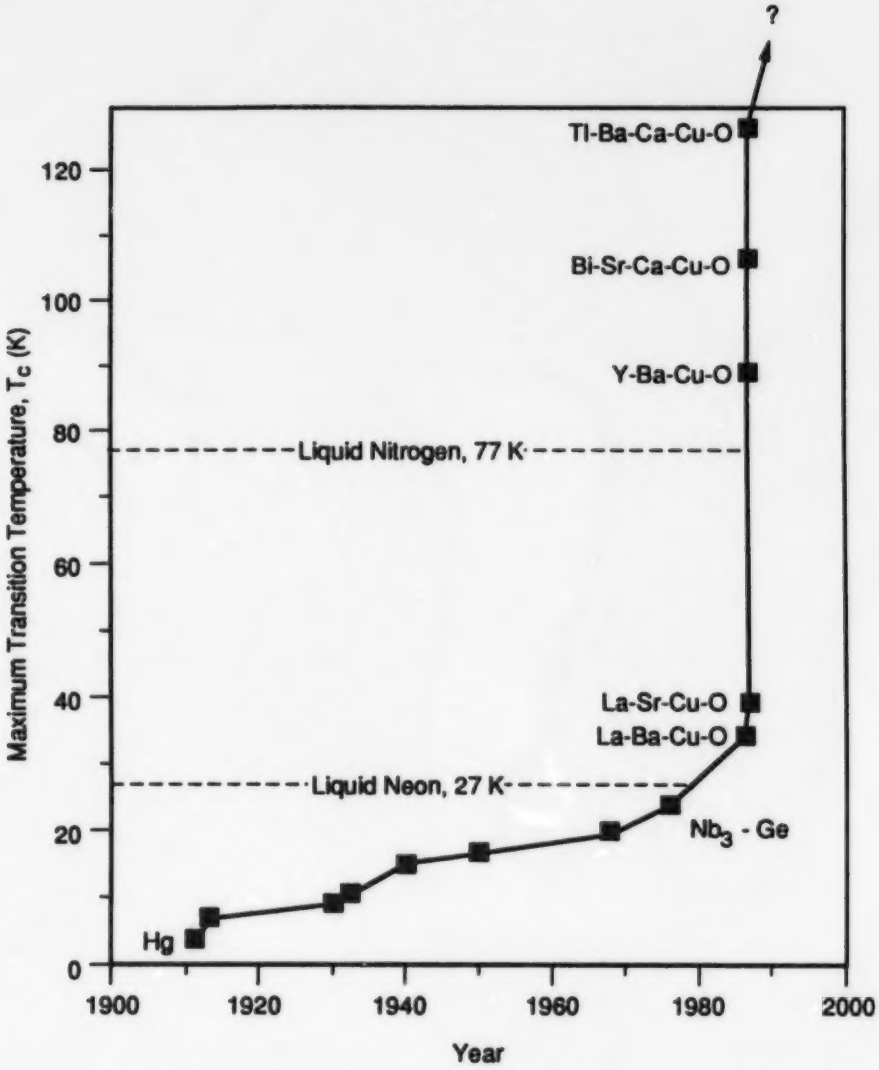


FIGURE A3

TRANSITION TEMPERATURE OF SUPERCONDUCTIVE COMPOUNDS AND THEIR YEAR OF DISCOVERY

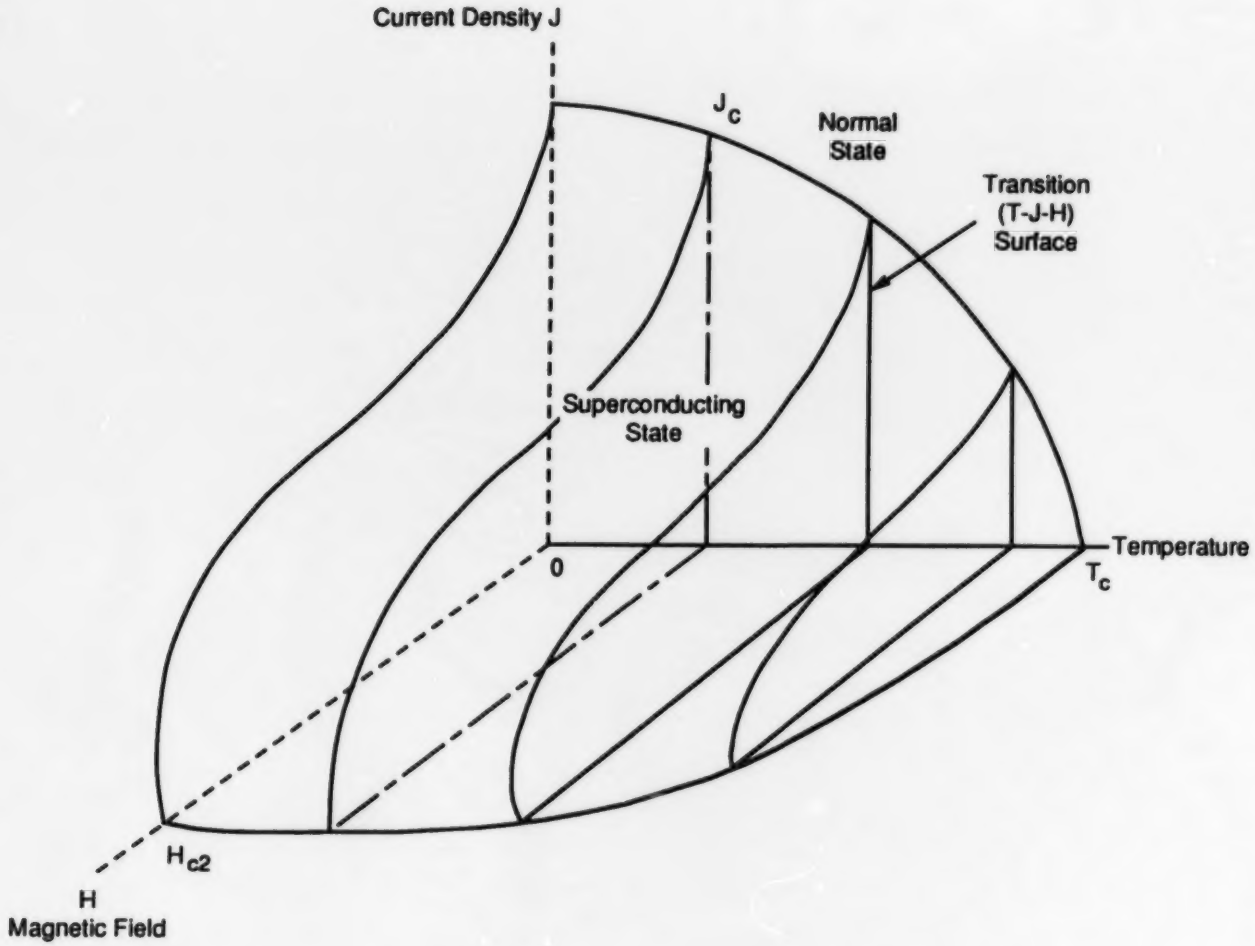


FIGURE A4

TRANSITION SURFACE FROM THE SUPERCONDUCTING TO THE NORMAL STATE

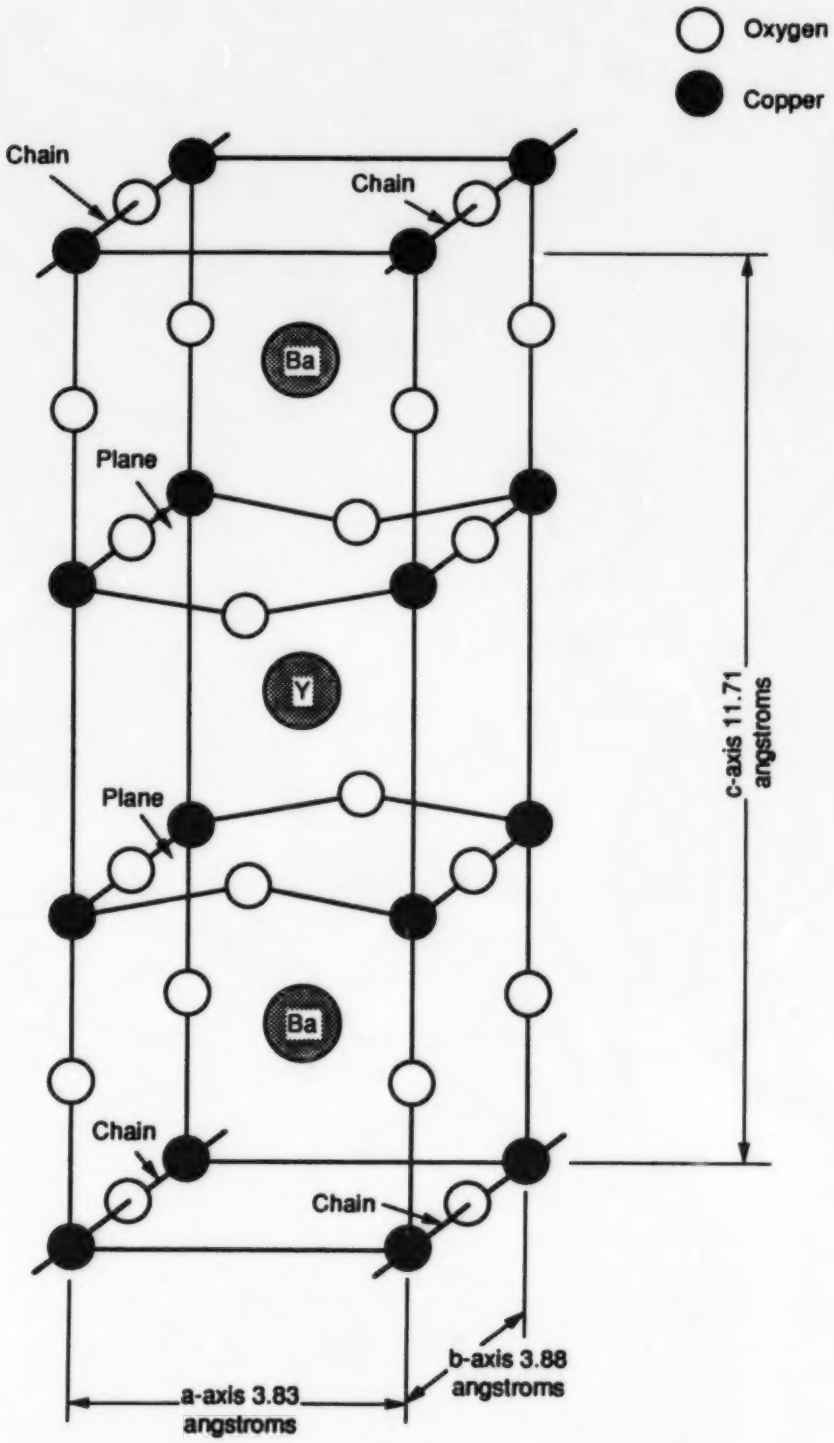


FIGURE A5

THE BASIC CELL OF THE CRYSTALLINE YTTRIUM-BARIUM-COPPER OXIDE SUPERCONDUCTOR

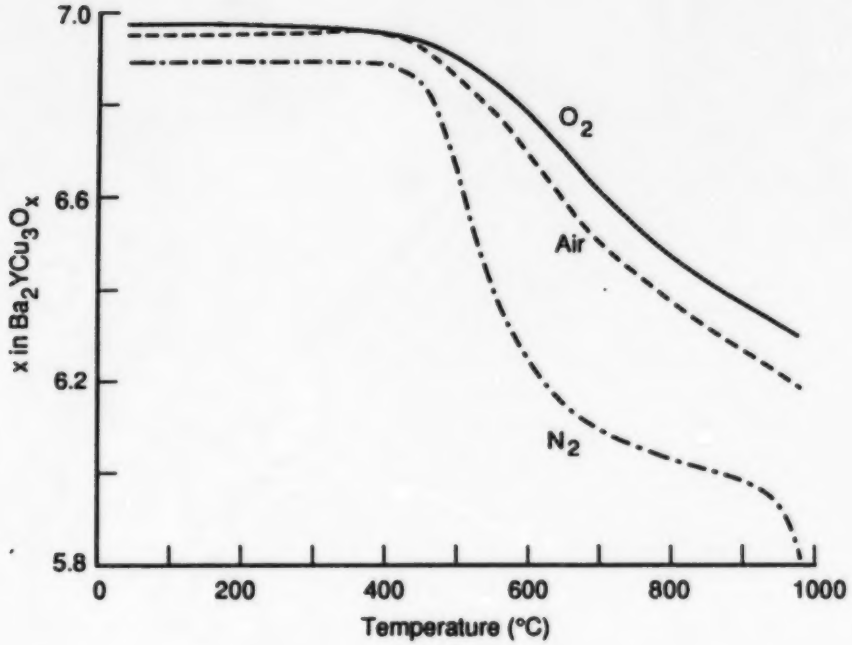


FIGURE A6

THE OXYGEN STOICHIOMETRY AS A FUNCTION OF TEMPERATURE IN O_2 , AIR, AND N_2 OBTAINED BY THERMOGRAVIMETRY. WEIGHT CHANGES ARE REVERSIBLE IN O_2 AND AIR

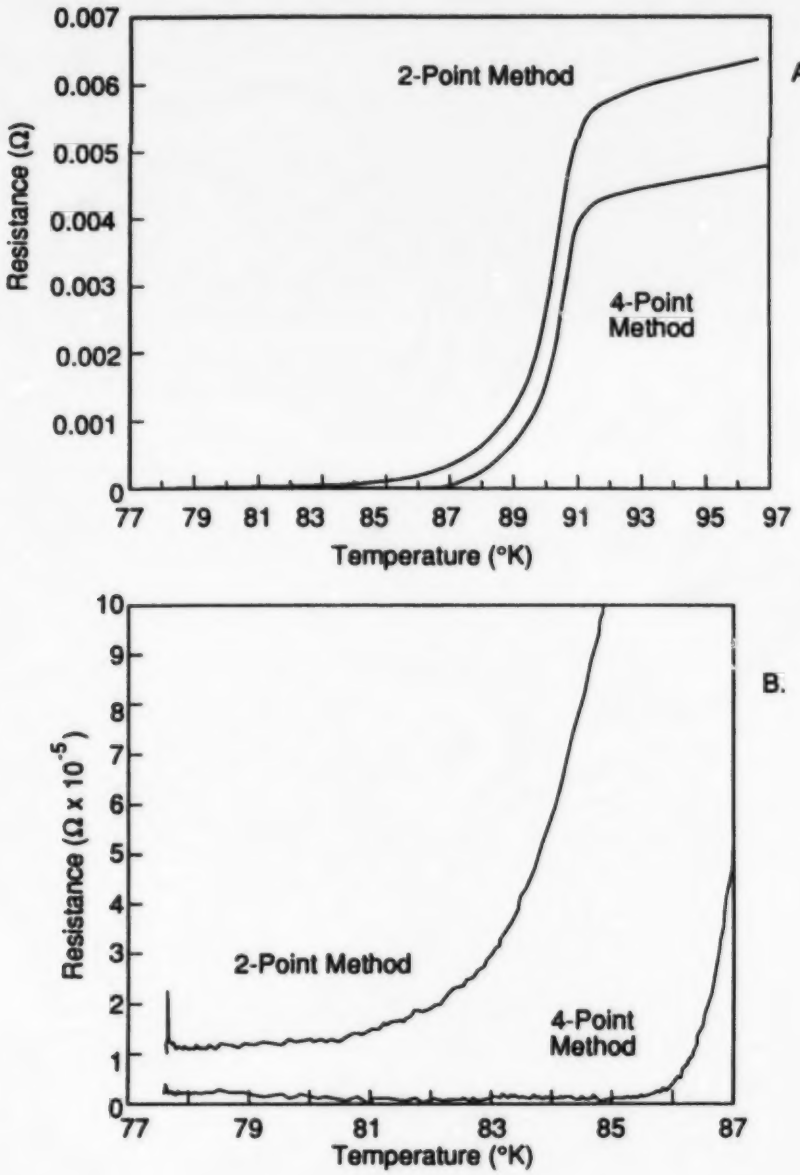


FIGURE B1

COMPARISON OF RESISTANCE OF METALLIZED 1-2-3 SAMPLE MEASURED AS A FUNCTION OF TEMPERATURE BY 4-POINT AND 2-POINT METHODS

A. General Resistance vs. Temperature Curves by 4-Point and 2-Point Techniques

B. Details of Resistance vs. Temperature Curve Below T_c

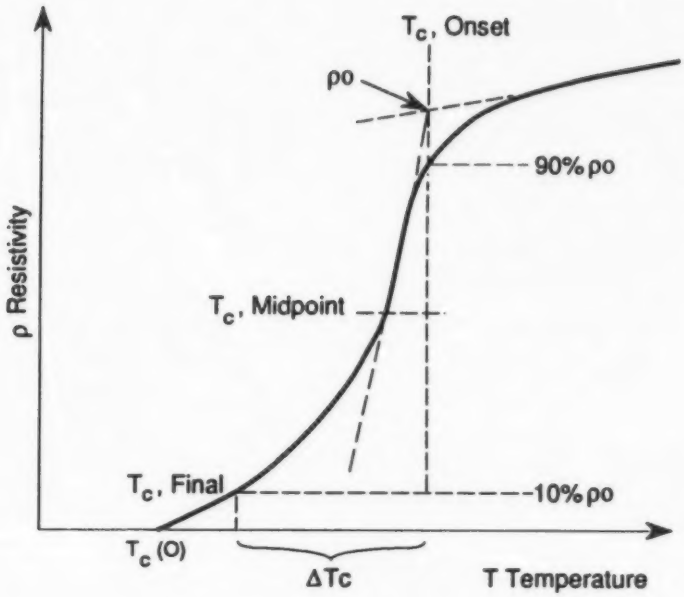


FIGURE B2

DEFINITION OF CRITICAL TEMPERATURE (T_c) BY 4-PROBE METHOD

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APPENDIX A

BACKGROUND INFORMATION

A.1 Superconductive Materials - Short History.

Superconductivity is the ability of certain materials, when cooled to extremely low temperatures, to conduct a direct electrical current with no resistance and hence no power loss. This phenomenon was discovered in 1911 when H.K. Onnes, investigating the effects of very low temperatures on metals behaviour, found that the resistivity of mercury disappeared suddenly when it was cooled to 4 K. Figure A1 illustrates this phenomenon/2/. Onnes called this property superconductivity, and he soon found that other metals, including tin and lead, exhibited superconducting properties at very low temperatures. Figure A2 shows schematically the changes in resistivity for normal metals and superconductors as a function of temperature.

Despite the great expectations for new electric superconducting machinery that would operate without loss, in only two years after H.K. Onnes'original discovery the interest in large scale commercial applications had begin to wane. Soon it was learned that the superconducting behaviour of these elemental superconductors, classified as Type I, was quenched by small current densities and ordinary levels of magnetic fields. The disappointment that followed was quite premature. In 1933 W. Meissner and R. Ochsenfeld discovered that the superconductors not only excluded but expelled the magnetic flux. This discovery contributed to the development of the understanding and practical applications of these materials.

During 1950s a new class of superconductors, classified as Type ll, was discovered. These materials, that consist mainly of niobium and its alloys, such as tin-niobium and niobium-titanium, were able to carry enormous current and to operate in high magnetic flux. For example, in ductile niobium-titanium wires current densities of 100,000 A/cm^2 are achieved at fields of 800,000 gauss. A large number of engineering applications based on superconductive materials became possible. However, most of these possibilities remained dreams, since liquid helium cooling system required to achieve the critical temperature, proved too costly for most applications/3/. As a result, early low transition temperature superconductors were only practical for certain specialized applications such as medical diagnostic instruments and particle accelerators for high-energy physics experiments. Figure A3 illustrates in a graphical form the history of discovery of superconductive compounds and their critical temperature.

Dream and hopes of finding materials with higher superconducting temperature were renewed in 1986, when an unexpected breakthrough occurred. K.A. Muller and J.G. Bednorz of IBM's Zurich research laboratories discovered that a ceramic material, lanthanum barium copper oxide, becomes superconductor at 30 K. IBM announcements, confirming this discovery and identifying other oxide superconductors, followed. By February 1987, Paul Chu and M.K. Wu's discovery of yttrium barium copper oxide superconducting at 95 K brought the transition temperature into the range of 'iquid nitrogen cooling. The discovery of these ceramic superconductors initiated a new era, that of the high temperature superconductors, since the liquid helium which boils at 4 K was no more required.

A.2. High Temperature Superconductive Materials.

A.2.1. Definition and Classification

Presently, HTSC materials are defined as ceramic compounds consisting of complex oxides that exhibit superconducting behaviour above 25 K. To date, the HTSC materials mainly belong to three classes of compounds/3/. The first class of HTSC consists of compounds that have an oxygen-deficit perovskite-like structure and contain copper-oxygen planes. As single crystals, these compounds are highly anisotropic since their superconductivity occurs in the copper-oxygen planes. Most of the ceramic superconductors discovered to date, such as La-Ba-Cu-O, La-Sr-Cu-O, Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O and Tl-Ca-Ba-Cu-O belong to this class of superconductors. In 1988 scientists from Bell Laboratories discovered the second type of ceramic superconducting compounds, those that contained no copper. The first compound belonging to this class had a transition temperature of 30 K and consisted of barium, potassium, bismuth and oxygen. Unlike the copper containing superconductors, these compounds exhibited superconductivity in three directions, rather than being restricted to a plane in the unit crystal. It appears possible that the discovery of this type of compounds will lead to a new class of isotropic superconductors. The last class of superconductors, known also as "superconducting smorgasbord", contains compounds that consist of lead, strontium, copper, oxygen and another element that belongs to the rare earth metals. Since there is a large number of possible combinations of these elements it is believed that ceramic compounds with improved superconducting properties belonging to this class are to be discovered in the near future/3/.

A.2.2. General Considerations

An all-inclusive explanation of high temperature superconductivity has not yet been developed. However, the basic, generally accepted theory of superconductivity postulates that under supercooled conditions, electrons, which normally repel each other, develop a mutual attraction and form pairs called Cooper pairs. For superconductivity to occur the electrons must be able to travel in a conductor without encountering any resistance from atomic vibrations and crystal imperfections. When one electron of a Cooper pair strikes an obstacle, the other electron responds by moving in the opposite direction so no energy is lost between the two. If enough Cooper pairs form, they may coalesce into a stream of freely moving electrons that can carry direct electrical current indefinitely, resulting in superconductivity.

The state of a superconducting material is determined by three critical parameters: temperature, current density and magnetic field strength. For each superconductor there is a critical temperature (T_c) at which normal conductivity changes to superconductivity, a critical magnetic field (H_c), which, when exceeded, will destroy the superconductivity and a critical current density (J_c) that when transported through it will cause quenching of the material. Therefore, from the point of view of engineering applications, the operating region for a superconductor may be considered as lying below a temperature-current density-magnetic field surface, as illustrated in Figure A4. This graphs indicates that the higher one of these properties is, the lower one or both of the other properties must be for the material to maintain its superconducting property.

Since the critical temperature is the temperature at which thermal energy is sufficient to destroy the relatively weak bonds between the electrons of Cooper pairs, the superconductivity in classical metallic materials occurs at low temperatures. The nature of the bond responsible for

superconductivity in oxide system is still not understood since the higher transition temperature that characterizes them implies a stronger bond of the Cooper pairs.

For most of the electric power applications, it is essential that the ceramic superconductors have high critical densities up to 300,000 A/cm^2. However, the majority of the bulk ceramic superconductors have a very poor current carrying capacity. In bulk materials the values of J_c ranging up to 1100 A/cm^2 are usually observed. The current carrying capacity is still lower in applied magnetic fields. If critical current density cannot be significantly increased, equipment based on HTSC materials should incorporate wires with large cross sections. This would result in heavy,inflexible and expensive components that would cancel most of the benefits of using HTSC materials.

Consequently, scientists around the world are trying to understand the reasons for which the ceramic superconductors have a very low critical current density and show a much stronger dependence on the applied magnetic field than would be expected. To date, it is well established that in a polycrystalline ceramic material consisting of a large number of anisotropic and randomly oriented grains,the current will flow in a tortuous path, similar to a percolation phenomenon. It is also believed that the grains are surrounded by non-superconducting boundaries that would therefore act as barriers. This phenomena is generally known as weak link effect. There are several explanations of this phenomenon/4/:

1. Impurities, particularly carbon, that accumulate at grain boundaries.

2. Stoichiometry that is different at the grain boundaries than in the grains.

3. Microcracks formed at grain boundaries with an unsuitable orientation.

4. Twin boundaries formed during superconductor processing.

Based on this understanding, several processing techniques that produced texturized $YBa_2Cu_3O_{7-x}$ materials with superior current carrying capacity were developed recently. A liquid phase processing method developed by Salama et al./5/ produced this ceramic superconductor with an oriented grain structure which carried direct current in excess of 18500 A/cm^2 and up to 75,000 A/cm^2 with a dc pulse measurement technique in zero field at 77 K.

Furthermore, a new fabrication method was developed at Bell Laboratories to overcome another major problem in ceramic superconductors, that of pinning centres. The lack of flux pinning and movement of magnetic flux in a HTSC material cause current dissipation and therefore resistance. Therefore, the motion of the magnetic flux was inhibited by the pinning centres created by small defects introduced in $YBa_2Cu_3O_{7-x}$ samples during their exposure to high-energy neutrons; before irradiation the maximum current the crystal could carry without losing its superconductivity was 6,500 A/cm^2, while after treatment the critical current density jumped to 620,000 A/cm^2 at 77 K/6/.

This evidence indicates that the understanding of detailed mechanism of superconductivity in ceramic oxides will lead to practical solutions that will make possible the use of HTSC materials in a very near future.

A.2.3 $YBa_2Cu_3O_{7-x}$ Compound

The first of the new HTSC to receive detailed attention was $YBa_2Cu_3O_{7-x}$ compound, popularly known as 1-2-3. The structure of this compound is similar to that of the ideal perovskite structure, which consists of cubes of three distinct elements with a chemical formula AMO_3, where A-cations occupy the centres of the cube, M-cations occupy corners, and O-anions occupy the centres of the edges of the cube. The 1-2-3 compound has an extensive oxygen deficiency with yttrium and barium occupying A-cation sites and copper filling M-cation sites. There is no oxygen in the yttrium layer, and less than one-half of the oxygen sites in the basal planes are occupied. Figure A5 shows the molecular structure of oxygen deficient perovskite.

The superconductive properties of this compound depend on its stoichiometry. Neutron scattering studies indicate that 1-2-3 materials have molecular structure that are either orthorhombic or tetragonal, depending on oxygen stoichiometry. For values of less than 0.6 the compound is orthorhombic, while for values larger than 0.6 a transition to a tetragonal structure occurs. Only the orthorhombic structure exhibits superconductivity. Figure A6 illustrates the effect of stoichiometry on critical temperature of this compound. The tetragonal phase remains stable at room temperature when oxygen content is lower than 6.45; in air the transition from tetragonal to orthorhombic structure occurs around 950 K with oxygen content close to 6.6/7/.

Transition from tetragonal to orthorhombic structure is accompanied by formation of planar defects that most probably are transformation twins. Presence of twinning boundaries in 1-2-3 materials adversely affects the critical current density in these compounds since they form effective intergrain weak-links.

From a materials engineering point of view the 1-2-3 superconductor/4/ is a difficult material. It is brittle ceramic and cleaves readily along the basal plane. Its fracture toughness is affected by the water vapours. These properties together with poor current carrying capacity indicate that careful processing and engineering of this material into a practical conductor are required for its use in electrical industry.

A.2.4 Concluding Remarks

Based on this brief review, it emerges that the progress in the area of the practical applications based on HTSC materials will occur through research in the following areas:

<u>Fundamental Research</u>

- structure of HTSC materials,
- connection between structure and superconductivity,
- understanding of superconductive mechanism and
- identifying new superconductive compounds

<u>Critical Properties</u>

- correlations between microstructure and critical values
- improvement of critical property values required for specific practical applications.

Applications

- processing bulk, thin film and single crystal HTSC materials with improved critical properties
- fabricate practical superconductors, wires, cables and devices.
- discover new areas for practical applications of superconductors.

Consequently, our investigation is related to a HTSC topic that has received very little attention until recently, namely that of the interfaces that are being generated when the ceramic materials are joining the metals.

APPENDIX B

MEASUREMENT OF ELECTRICAL PROPERTIES OF METALLIZED SAMPLES

B.1 Contact Resistivity

For most applications of HTSC materials requiring high current carrying capacity, the achievement of a low resistance electrical 1-2-3/metal conductor contact is essential. Furthermore, fabrication of metallized samples with low contact is also an essential requirement in the laboratory evaluation of the current carrying capacity (J_c) and resistance measurement of critical temperature of the superconductor material. Therefore, to characterize the different metallizing techniques that were used to deposit the silver contact on 1-2-3 sample, the contact resistivity was measured. Figures B1 A and B1 B illustrate the general principle used evaluate the electrical resistivity of 1-2-3/Ag contacts. The resistance of the metallized sample was measured as a function of temperature by the both, 4-point and 2-point (for an average value of contact resistivity), or 3-point methods (for the value of individual contacts) as shown in Figure B1 A. The difference between the two curves represents the contribution of contact resistivity. The details of the resistance versus temperature curve for temperature below the Tc are shown in Figure B1 B. From this graph an average contact resistivity of $4.5 \times 10^{-7} \Omega.cm^2$ was calculated. Since the values of the contact resistivity for most of our samples were much lower than that illustrated for exemplification in Figure B1, practically, we measured the voltage across the sample, with and without the current supply, to eliminate the offset voltage of the digital multimeter. From the voltage value, the resistance was calculated, accordingly. The contact resistivity is obtained by multiplying this contact resistance with the contact area.

B.2 Critical Temperature

Figure B2 shows the experimental approach that was used/18/ to define the T_c measured by four-probe technique such that our results could be compared with data from literature and with those for samples prepared by laboratories outside Ontario Hydro. From the resistivity-temperature graph the values for ρ_o, T_c onset, T_c midpoint, T_c final and ΔT could be established for each investigated sample. ρ_o is the resistivity of the HTSC just above its T_c and ΔT_c represents the temperature width and is graphically is defined as the point of intersection of extrapolated normal resistivity line and the line through the sharpest part of the superconducting-normal transition (steepest slope).

T_c onset is determined as the point at 90% ρ_o on the resistivity versus temperature curve, the T_c midpoint is evaluated as the point at 50% ρ_o and the T_c final is the point at 10% ρ_o on the same curve. ΔT_c is the difference between the T_c onset and T_c final. The $T_c(0)$ is considered as the temperature at which a voltage of $1\mu V$ is detected.